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PROCESS FOR DEVELOPING SILVER HALIDE COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIALS AT HIGH TEMPERATURE

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Int. Cl. G03c *5/30*
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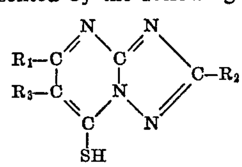
ABSTRACT OF THE DISCLOSURE

A developing process which comprises subjecting a multi-layer silver halide color photographic material to high temperature processings in the presence of a compound represented by the following general formula



wherein R_1 and R_2, which may be the same or different, each represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, or a haloaryl group, and R_3 represents hydrogen atom, a halogen atom, or an alkyl group is disclosed.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a process for developing color photographic materials. More particularly, the present invention relates to a rapid developing process for color photographic material at high temperatures.

(2) Description of the prior art

A multiple layer color photographic material has at least three superposed silver halide emulsion layers having different spectral sensitivities on a support. For instance, in the case of a typical color photographic material, a red-sensitive emulsion layer, a green-sensitive emulsion layer, a yellow filter layer, and a blue-sensitive emulsion layer are coated on a support in this order.

One aspect of the progress in recent photographic processing engineering is the speeding up of processing by raising the temperature of development (higher than 30° C.). This is usually called "high temperature rapid processing." One of the disadvantages occurring in the high temperature rapid processing of multi-layer color materials is that the uppermost layer is developed excessively before the bottom layers are completely developed.

It is known that to overcome this drawback a development inhibitor is added to the developing solution. However, when the development inhibitor which has usually been used, such as a 6-nitro-iso-indazole compound, is added to a developing solution, not only is the development of the uppermost layer inhibited but that of the bottom emulsion layers also is inhibited.

In order to avoid this disadvantage, the addition of an acyl-amino-phenyl mercaptotetrazole compound to a developing solution or a photographic emulsion layer is known to be effective, because the development of the uppermost layer is selectively inhibited by the compound and the balance of the entire development is improved (see U.S. Pat. No. 3,295,976). However, the mercaptotetrazole compound described in this patent has the difficulty in its synthesis since the raw material for the compound is thiophosgene which is generally difficultly available.

An object of this invention is to provide a high temperature-rapid development process for multiple layer silver halide color photographic materials using an effective development inhibitor for the uppermost layer.

SUMMARY OF THE INVENTION

As the result of investigations of various compounds we have discovered that the desired effect can be obtained by adding to the developing solution a mercaptotetraazaindene compound which can be readily synthesized.

According to the present invention, by adding a mercaptotetraazaindene compound to a developing solution or to a bath preceding the development, such as a prehardening bath or a neutralizing bath, it is possible to inhibit selectively the development of the uppermost layer of a multiple layer color photographic material, and to prevent the uppermost layer from being excessively developed, and to improve the total color balance and the image quality.

DETAILED DESCRIPTION OF THE INVENTION

As a processing solution prior to the development, there is usually employed a pre-hardening bath, that is, an aqueous solution containing an aldehyde for hardening the gelatin in a photographic emulsion layer, such as formaldehyde, glyoxal, succinaldehyde, glutaraldehyde, and the like. The aqueous solution further contains a salt such as sodium sulfate, a pH-controlling agent or a buffer agent, such as borax, boric acid, acetic acid, sodium acetate, sodium hydroxide, sulfuric acid, and the like, and also an antifoggant for development, such as an alkali metal halide. The development inhibitor of this invention can be added to such an aqueous pre-hardening solution.

When a neutralizing bath is employed for preventing the aldehyde in the pre-hardening bath from being carried in the developing solution, the development inhibitor of this invention can be added to the neutralizing bath. The neutralizing bath contains an aldehyde-scavenging agent, such as hydroxylamine and L-ascorbic acid, and it can further contain a salt and a pH-controlling agent or a buffer agent.

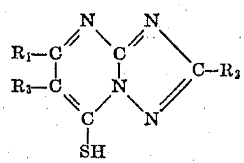
The black & white developing solution for reversal color photographic films contain at least one of the developing agents such as hydroquinone, 1-phenyl-3-pyrazolidone and N-methyl-p-aminophenol. The developing solution further contains a salt such as soduim sulfate, a pH-controlling agent or a buffer agent such as borax, boric acid, sodium hydroxide, sodium carbonate, and the like, and an alkalimetal halide. The development inhibitor of this invention can also be added to the black and white developing solution.

As a color developing solution for color negative films and color papers, there is usually used as alkaline aqueous solution containing a p-phenylene-diamine derivative as a color developing agent, such as

N,N-diethyl-p-phenylene-diamine sulfite,
N,N-diethyl-3-methyl-p-phenylenediamine hydrochloride,
4-amino-3-methyl-N-ethyl-N-methanesulfoamidoethyl aniline sulfate,
4-amino-3-methyl-N-ethyl-N-hydroxyethyl aniline sulfate,
N-ethyl-N-hydroxyethyl-p-phenylene-diamine sulfate,

and the like. The solution further contains a salt such as sodium sulfate, a pH-controlling agent or a buffer agent such as sodium hydroxide, sodium carbonate, sodium phosphate, and the like, and a conventional antifoggant such as an alkali metal halide. The developing inhibitor of this invention can be added to the color development solution.

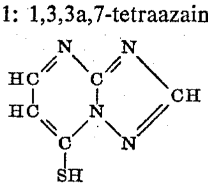
The objects of this invention are attained by adding a mercaptotetraazaindene compound represented by the following general formula



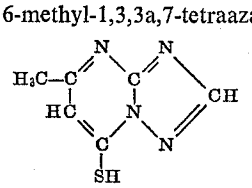
wherein R_1 and R_2, which may be the same or different, each represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group or a haloaryl group and R_3 represents a hydrogen atom, a halogen atom or an alkyl group, to any of the above-described processing solutions.

Typical examples of the compounds to be used in the invention represented by the above general formula are shown below although the scope of this invention is not to be interpreted as being limited to these compounds.

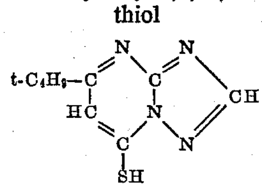
Compound 1: 1,3,3a,7-tetraazaindene-4-thiol



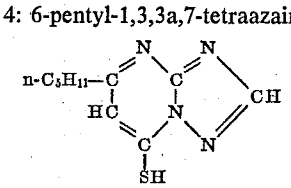
Compound 2: 6-methyl-1,3,3a,7-tetraazaindene-4-thiol



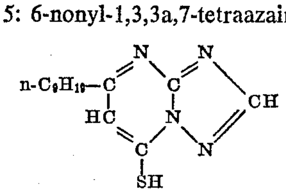
Compound 3: 6-tertiary-butyl-1,3,3a,7-tetraazaindene-4-thiol



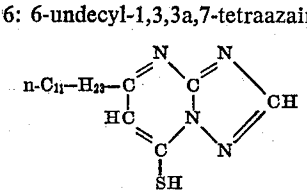
Compound 4: 6-pentyl-1,3,3a,7-tetraazaindene-4-thiol



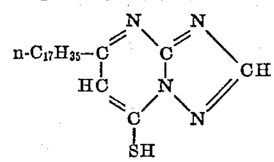
Compound 5: 6-nonyl-1,3,3a,7-tetraazaindene-4-thiol



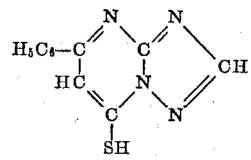
Compound 6: 6-undecyl-1,3,3a,7-tetraazaindene-4-thiol



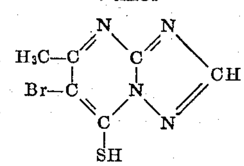
Compound 7: 6-heptadecyl-1,3,3a,7-tetraazaindene-4-thiol



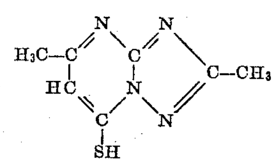
Compound 8: 6-phenyl-1,3,3a,7-tetraazaindene-4-thiol



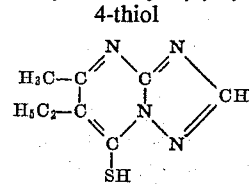
Compound 9: 5-bromo-6-methyl-1,3,3a,7-tetraazaindene-4-thiol



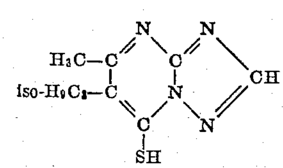
Compound 10: 2,6-dimethyl-1,3,3a,7-tetraazaindene-4-thiol



Compound 11: 5-ethyl-6-methyl-1,3,3a,7-tetraazaindene-4-thiol



Compound 12: 5-iso-butyl-6-methyl-1,3,3a,7-tetra-azaindene-4-thiol



The compound represented by the above-described general formula can generally be prepared by reaction of aminotriazole with an acylacetic acid ester, the product then being reacted with phosphorus oxychloride, and after extraction, the extract being reacted with thiourea.

SYNTHESIS EXAMPLE

(Compound 3)

Aminotriazole and an equimolar amount of 4,4-dimethyl-3-oxo-valeric acid ethyl ester were heated for 7 hours in glacial acetic acid and when the crystal thus formed was recrystallized from methanol, 4-hydroxy-6-tertiary-butyl-1,3,3a,7-tetraazaindene having a melting point of 269° C., was obtained. After reacting the tetraazaindene with phosphorus oxychloride for 1 hour at 120° C., the product was poured in ice-water and then extracted with methylene chloride. When the crystals of the 4-chloro compound obtained were reacted with thiourea in ethanol and the crystals thus formed were re-crystallized from alcohol, acicular needle-like crystals of 6-tertiary-butyl-1,3,3a,7-tetraazaindene having a melting point of 286° C. was obtained.

Other compounds can also be synthesized by the process described in the specification of British Pat. No. 893,428.

It is disclosed in the specification of British Pat. No. 893,428, that by adding the compound represented by the general formula above to a silver halide, the storage-stability of the silver-halide on storage was improved and the thermal stability of the silver image obtained was increased. However, the use of the compound in this invention is fundamentally different from the disclosure of the British patent. That is to say, in the case of subjecting a color photographic light-sensitive material to high temperature processings, such phenomena frequently occur that the uppermost layer thereof is excessively developed and a change of color balance occurs. In this case, with high temperature development in the presence of the compound of the present invention, an image having improved color balance can be obtained without being accompanied by such disadvantages. Thus, it can be said that the high temperature processing for color photographic light sensitive materials cannot be practiced effectively without employing the process of this invention. Each of the compounds represented by the general formula set forth above can prevent the excessive development of the surface layer or the uppermost emulsion layer and development processing giving good color balance can be conducted. Among these compounds, however, compound 3 can give the best results.

The amount of the compound of this invention to be employed can be varied according to the type of the compound, the type of color photographic material to be used, and the nature of the composition of the processing solution. In general, however, the amount of compound used can range from 1 mg. to 1 g. per liter of the processing solution.

The optimum amount of the compound depends upon many factors, such as the compound to be employed, the composition of the processing solution, the activity of the developing solution, the processing temperature, and the properties of the multiple layer color photographic light-sensitive material.

The invention will be explained below in greater detail by reference to the following example.

EXAMPLE 1

A multi-layer color reversal film composed of three silver halide emulsion layers contain different couplers and having different spectral sensitivities was exposed using a sensitometer and then subjected to the following procedures.

Process	Temperature, ° C.	Time
Black and white development	37	3 min.
First stopping	37	30 sec.
Water washing	37	1 min.
Color development	37	3 min. and 30 sec.
Second stopping	37	30 sec.
Water washing	37	1 min.
Bleaching	37	1 min. and 30 sec.
Fixing	37	1 min.
Water washing	37	1 min.

The compositions of the processing solutions used in the above processings were as set forth below:

Black & white developing solutions:

Sodium hexa-metaphosphate	g	1.0
1 - phenyl - 3 - pyrazolidone	g	0.3
Sodium sulfite	g	50.0
Hydroquinone	g	6.0
Sodium carbonate (monohydrate)	g	35.0
Potassium bromide	g	2.0
Potassium thiocyanate	g	1.0
Potassium iodide (0.1% aqueous solution	cc	10.0
Water added to make 1 liter.		

First and second stopping solution:

Acid acid	cc	25
Sodium acetate	g	25
Water added to make 1 liter.		

Color developing solution:

Sodium hexameta-phosphate	g	1.0
Benzyl alcohol	cc	6.0
Sodium sulfite	g	5.0
Sodium phosphate	g	40.0
Potassium bromide	g	0.2
Potassium iodide (0.1% aqueous solution	cc	10.0
Sodium hydroxide	g	6.5
4 - amino - 3 - methyl - N - ethyl-N-methanesulfonamidoethyl aniline sulfate	g	10.0
Ethylenediamine	cc	8.0
Water added to make 1 litter.		

Bleaching solution:

Ferricyaninde	g	100
Potassium bromide	g	30.0
Water added to make 1 liter.		

Fixing solution:

Sodium thiosulfate	g	150
Sodium sulfite	g	10
Water added to make 1 liter.		

In the above-described reversal development processings, the compound of this invention was added to the black and white developing solution. For comparison, the same procedure was repeated using a black and white developing solution containing a conventionally known antifoggant, 6-nitrio-isoindazole instead of the compounds of this invention.

Test No.	Additives to black and white developing agent	Amount of additive
1	None	
2	Compound 1	2.0×10^{-5} mole/liter.
3	Compound 3	Do.
4	6-nitroisoindazole	Do.
5	do	5.0×10^{-4} mole/liter.

The results obtained are shown in the following table, in which the blue density ($D_{B\text{-max}}$) and red density ($D_{R\text{-max}}$) of the unexposed part of the test strips (maximum density part) and sensitivities for red and blue exposures are listed to indicate the photographic effect.

Test No.	Maximum density		Sensitivity [1]	
	Blue density	Red density	Blue	Red
1	2.4	3.4	175	115
2	3.4	3.5	100	100
3	3.5	3.6	99	98
4	2.5	3.4	150	105
5	3.7	3.7	70	72

[1] The sensitivity was determined relatively by assuming the sensitivity of Test No. 2 being 100.

As shown in the above table, the addition of the compound of this invention, a good image quality having a sufficiently high blue density and a good balance of blue density and red density was obtained without reducing the sensitivity. On the other hand, in the experiment of using 6-nitroisoindazole instead of the compound of this invention, it was confirmed that if the amount of it was small, the effect of increasing the blue density was small and if the amount is large, the sensitivity was greatly reduced although the blue density increased, thereby good image quality was not obtained. In other words, with the known developing inhibitor, the development of both the uppermost layer and the bottom layers were inhibited. On the other hand, using the compound of this invention, the excessive development of the uppermost layer by the high temperature development was prevented, the development was conducted with a good balance, and no reduction in sensitivity occurred as shown in the above-described table.

EXAMPLE 2

A multiple layer color photographic film prepared by coating a cellulosive triacetate film with a red-sensitive gelatino silver iodobromide emulsion layer, a green-sensitive gelatino silver iodobromide emulsion layer, a colloidal silver-containing gelatino yellow filter having blue absorption, and a blue-sensitive gelatino silver iodobromide emulsion layer successively was exposed using a sensitometer and then subjected to the following processing.

Process	Temperature, ° C.	Time
Pre-hardening	40	30 sec.
Water washing	40	Do.
First black and white development	40	75 sec.
Water washing	40	30 sec.
Reversal exposure (red light) from the back face of the film		200 cms.
Cyan color development	40	180 sec
Water washing	40	30 sec.
Rev ersal exposure (blue light) from the front face of the film		200 cms.
Yellow color development	40	90 sec.
Water washing	40	30 sec.
Second black and white development	40	15 sec.
Magenta color development	40	120 sec.
Water washing	40	60 sec.
Bleaching	40	Do.
Fixing	40	Do.
Water washing	40	Do.

The compositions of the processing solutions used above were as set forth below.

Hardening solution:

Sodium hexa-metaphosphate	g	1.0
Soduim pyrosulfite	g	5.0
Sodium pyrophosphate	g	15.0
Sodium sulfate	g	150.0
Potassium bromide	g	2.0
Sodium hydroxide	g	0.1
Formalin (37%)	cc	15.0

Water added to make 1 liter.

First black & white developing solutions:

N-methyl-p-aminophenol	g	5.0
Sodium sulfite	g	70.0
Hydroquinone	g	2.0
Sodium carbonate (monohydrate)	g	41.0
Potassium bromide	g	4.0
Potassium thiocyanate	g	1.6
Potassium iodide (0.1% aqueous solution)	cc	10.0

Water added to make 1 liter.

Cyan color developing solution:

Potassium bromide	g	3.0
6-nitrobenzimidazole	g	0.03
Potassium iodide (0.1% aqueous solution)	cc	10.0
Sodium sulfite	g	10.0
Sodium sulfate	g	60.0
Potassium thiocyanate	g	1.0
4-amino-3-methyl-N-ethyl-N-hydroxyethyl aniline sulfate	g	2.5
Sodium hydroxide	g	3.0
1,5-dihydroxy-2,6-dibromonaphthalene	g	2.0
Monobenzyl-p-aminophenol	g	0.4
p-Aminophenol hydrochloride	g	0.1

Water added to make 1 liter.

Yellow color development:

Sodium sulfite	g	10.0
Potassium bromide	g	0.5
Potassium iodide (0.1% aqueous solution)	cc	25.0
6-nitrobenzimidazole	g	0.1
Sodium sulfate	g	60.0
N,N-diethyl-p-phenylenediamine sulfite	g	2.5
Sodium hydroxide	g	2.5
ω-Benzyl-4-(p-toluenesulfoamido)-acetanilide	g	1.8

Water added to make 1 liter.

Second black and white developing solution:

N-methyl-p-aminophenol sulfate	g	1.0
Sodium sulfite	g	50.0
Hydroquinone	g	1.0
Sodium carbonate (monohydrate)	g	41.0
Potassium bromide	g	2.5

Water added to make 1 liter.

Magenta color developing solution:

Sodium sulfite	g	5.0
Potassium bromide	g	1.0
Potassium thiocyanate	g	1.0
Sodium sulfate	g	60.0
N,N-diethyl-3-methyl-p-phenylenediamine hydrochloride	g	2.5
Sodium hydroxide	g	2.0
1-phenyl-3-(m-nitrobenzoylamino)-5-pyrazolone	g	1.4
Ethylenediamine	cc	8.0

Water added to make 1 liter.

Bleaching solution:

Ferricyanide	g	100
Potassium bromide	g	30.0

Water added to make 1 liter.

Fixing solution:

Sodium thiosulfate	g	150
Sodium sulfite	g	10

Water added to make 1 liter.

In the above-described reversal development, the following composition of this invention was added to the prehardening solution.

Test No.	Additive to pre-hardening solution	Addition amount
1	None	
2	Compound 2	5.0×10^{-5} mole/liter.
3	Compound 4	Do.
4	Compound 5	Do.
5	Compound 6	Do.

The photographic properties obtained as a result of the development are shown in the following table. The blue density ($D_{B-max.}$) and the red density ($D_{R-max.}$) of the unexposed part of the strips (maximum density part) are shown as the photographic properties. The blue density is the density of the uppermost blue-sensitive emulsion layer of the film which gives the yellow color by color development and the red density is the density of the lower-most red-sensitive emulsion layer which gives the cyan. If the values are large and not so different from each other it means a good color balance and an image having good color reproduction.

Test No.	Blue density	Red density
1	2.3	3.5
2	3.6	3.5
3	3.6	3.6
4	3.3	3.6
5	3.2	3.5

As is clear from the table, by the addition of the compound of this invention, the blue density is increased without reducing the red density.

EXAMPLE 3

In the developing processings in Example 2, the compound of this invention was added to the first black & white developing solution, in this case, however, the compound of this invention was not added to the prehardening solution.

Test No.	Addition to first black and white developing solution	Addition amount
1	None	20×10^{-5} mole/liter.
2	Compound 7	Do.
3	Compound 8	Do.
4	Compound 10	Do.
5	Compound 11	Do.

The photographic properties obtained as a result of the development are shown in the following table. The blue density and the red density photographic properties are shown below.

Test No.	Blue density	Red density
1	2.3	3.5
2	3.5	3.7
3	3.6	3.6
4	3.7	3.6
5	3.6	3.6

As is clear from the table, by the addition of the compound of this invention the blue density is increased without reducing the red density.

EXAMPLE 4

A multiple layer type color photographic film consisting of three silver halide emulsion layers containing different couplers (cyan, yellow and magenta) and having different spectral sensitivities with each other was exposed by a sensitometer and then subjected to the following processings.

Process	Temperature, ° C.	Time
Color development	35	3 min.
Stopping	35	30 sec.
Water washing	35	Do.
Bleaching	35	1 min.
Fixing	35	90 sec.
Water washing	35	1 min.

The compositions of the processing solutions used above were as set forth below.

Color developing solution:

Sodium hexa-metaphosphate	g	1.0
Benzyl alcohol	g	5.0
Sodium sulfite	g	3.0
Sodium carbonate	g	41.0
Sodium hydroxide	g	1.0
4-amino-3-methyl-N-ethyl-N-methanesulfonamidoethyl aniline sulfate	g	5.0
Potassium bromide	g	0.5

Water added to make 1 liter.

Stopping solution:

Acetic acid	cc	25
Sodium acetate	g	3
Potassium alum	g	10

Water added to make 1 liter.

Bleaching solution:

Ferricyanide	g	100
Potassium bromide	g	20.0

Water added to make 1 liter.

Fixing solution:

Sodium thiosulfate	g	150
Sodium sulfite	g	10

Water added to make 1 liter.

In the negative color developing processings shown above, Compound 3 of this invention was added to the color developing solution in an amount of 5×10^{-5} mole/liter.

On comparing the results thus obtained with those in which no compound of this invention was added, it was confirmed that by the addition of the compound of this invention, the uppermost blue-sensitive emulsion layer was not excessively developed and the development could give good color balance among the red, green and blue densities.

EXAMPLE 5

In the developing processings in Example 1, a prehardening step and a neutralizing step were conducted before the first black & white development. The prehardening processing was conducted for 2 minutes and 30 seconds at 37° C. and the neutralizing process was carried out for 30 seconds at 37° C. The compositions of the processing solutions were as shown below.

Pre-hardening solution:

Formalin (37% aqueous solution)	cc	20
2,5-dimethoxytetrahydrofuran	cc	4
Sulfuric acid	cc	2
Sodium sulfate	g	100
Potassium bromide	g	2
Borax	g	5

Water added to make 1 liter.

Neutralizing solution:

Hydroxylamine sulfate	g	20
Potassium bromide	g	20
Glacial acetic acid	cc	10
Sodium sulfate	g	50
Sodium hydroxide	g	6

Water added to make 1 liter.

In the above-described reversal color development, the compound of this invention was added to the neutralizing solution as shown in the following table.

Test No.	Additive to neutralizing solution	Addition amount
1	None	
2	Compound 1	20×10^{-5} mole/liter.
3	Compound 2	Do.
4	Compound 5	Do.

The results obtained are shown in the following table, in which, as the photographic properties are shown the blue density and the red density at the maximum density and also the reversal sensitivity.

Test No.	Maximum density		Reversal sensitivity [1]	
	Blue density	Red density	Blue density	Red density
1	2.4	3.4	175	115
2	3.5	3.6	100	100
3	3.7	3.7	199	99
4	3.5	3.6	102	105

[1] The reversal sensitivity was shown by the relative sensitivity when the sensitivity of the test No. 2 was assumed to be 100.

As shown in the above table, by the addition of the compound of this invention, the blue density was fully increased without giving any influence on the sensitivity and an image having better blue and red color balance was obtained.

EXAMPLE 6

To any acetyl cellulose film were applied a red-sensitive gelatino silver iodobromide emulsion containing a phenolic cyan coupler and further an intermediate gelatin layer. Then, a green-sensitive gelatino silver bromide emulsion containing a pyrazolone magenta coupler was applied to the intermediate layer and further a yellow filter layer was formed on the layer. Then, a blue-sensitive gelatino silver iodobromide emulsion containing a keto-methylene yellow coupler was applied to the filter layer, and finally a protective gelatin layer was formed on the blue-sensitive emulsion layer.

Two kinds of the above-described color photographic films were prepared. One was a control sample and no compound of this invention was incorporated in any emulsion layers of the film but in the sample of this invention, 0.5 g./Ag mole of the Compound 3 of this invention was incorporated in the blue-sensitive emulsion layer of the photographic film.

The color photographic film thus prepared was exposed using a sensitometer and subjected to the color reversal development by the processings of Test No. 1 in Example 1. The results thus obtained are shown in the following table.

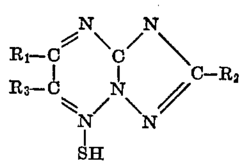
	Maximum density		Reversal sensitivity [1]	
	Blue density	Red density	Blue density	Red density
Control sample	2.3	3.3	145	106
Sample of invention	3.5	3.5	100	100

[1] The reversal sensitivity was shown by the relative sensitivity when the sensitivity obtained by the sample of this invention was assumed to be 100.

As shown in the above table, in the case of adding the compound of this invention, the blue density was sufficiently high even by the high temperature processings and an image having better color balance of the blue density and the red density was obtained.

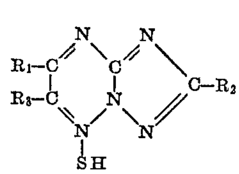
What is claimed is:

1. In a high temperature rapid processing developing process for color photographic material which comprises subjecting an exposed multi-layer silver halide color photographic material to development at a temperature higher than 30° C., the improvement which comprises selectively inhibiting development of the uppermost photographic emulsion layer to improve the color balance and image quality of the developed photographic material by processing said color photographic material no later than development in the presence of an effective development inhibitor for the uppermost photographic emulsion layer comprising a compound represented by general formula



wherein R_1 and R_2, which may be the same or different, each is selected from the group consisting of a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, and a haloaryl group, and wherein R_3 is selected from the group consisting of a hydrogen atom, a halogen atom, and an alkyl group.

2. In a high temperature rapid processing developing process for color photographic material comprising developing an exposed multi-layer silver halide color photographic material at a temperature higher than 30° C., the improvement which comprises selectively inhibiting the development of the uppermost photographic emulsion layer of said multi-layer silver halide color photographic material to improve the color balance and image quality of the developed photographic material by treating said photographic material no later than development with a solution containing an effective development inhibitor for the uppermost photographic emulsion layer comprising a compound represented by the formula



wherein R_1 and R_2, which may be the same or different, each is selected from the group consisting of a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, and a haloaryl group, and wherein R_3 is selected from the group consisting of a hydrogen atom, a halogen atom, and an aryl group.

3. The process as claimed in claim **2**, wherein said solution is a developing solution.

4. The process as claimed in claim **2**, wherein said solution is a pre-hardening solution.

5. The process as claimed in claim **2**, wherein said solution is a neutralizing solution.

6. The process as claimed in claim **2**, wherein said temperature is higher than 35° C.

7. The process as claimed in claim **1**, wherein said multi-layer silver halide color photographic material comprises a support having coated thereon, in succession, a red-sensitive photographic emulsion layer, a green-sensitive photographic emulsion layer, a yellow filter layer and a blue-sensitive photographic emulsion layer.

8. The process as claimed in claim **2**, wherein said multi-layer silver halide color photographic material comprises a support having coated thereon, in succession, a red-sensitive photographic emulsion layer, a green-sensitive photographic emulsion layer, a yellow filter layer and a blue-sensitive photographic emulsion layer.

9. The process as claimed in claim **3**, wherein said developing solution is a black and white developing solution.

10. The process as claimed in claim **3**, wherein said developing solution is a color developing solution.

11. The process as claimed in claim **1**, wherein said compound is selected from the group consisting of

1,3,3a,7-tetraazaindene-4-thiol,
6-methyl-1,3,3a,7-tetraazaindene-4-thiol,
6-tertiary-butyl-1,3,3a,7-tetraazaindene-4-thiol,
6-pentyl-1,3,3a,7-tetraazaindene-4-thiol,
6-nonyl-1,3,3a,7-tetraazaindene-4-thiol,
6-undecyl-1,3,3a,7-tetraazaindene-4-thiol,
6-heptadecyl-1,3,3a,7-tetraazaindene-4-thiol,
6-phenyl-1,3,3a,7-tetraazaindene-4-thiol,
5-bromo-6-methyl-1,3,3a,7-tetraazaindene-4-thiol,
2,6-dimethyl-1,3,3a,7-tetraazaindene-4-thiol,
5-ethyl-6-methyl-1,3,3a,7-tetraazaindene-4-thiol and
5-iso-butyl-6-methyl-1,3,3a,7-tetraazaindene-4-thiol.

12. The process as claimed in claim **2**, wherein said compound is selected from the group consisting of

1,3,3a,7-tetraazaindene-4-thiol,
6-methyl-1,3,3a,7-tetraazaindene-4-thiol,
6-tertiary-butyl-1,3,3a,7-tetraazaindene-4-thiol,
6-pentyl-1,3,3a,7-tetraazaindene-4-thiol,
6-nonyl-1,3,3a,7-tetraazaindene-4-thiol,
6-undecyl-1,3,3a,7-tetraazaindene-4-thiol,
6-heptadecyl-1,3,3a,7-tetraazaindene-4-thiol,
6-phenyl-1,3,3a,7-tetraazaindene-4-thiol,
5-bromo-6-methyl-1,3,3a,7-tetraazaindene-4-thiol,
2,6-dimethyl-1,3,3a,7-tetraazaindene-4-thiol,
5-ethyl-6-methyl-1,3,3a,7-tetraazaindene-4-thiol, and
5-iso-butyl-6-methyl-1,3,3a,1-tetraazaindene-4-thiol.

13. The process as claimed in claim **2**, wherein said solution contains said compound in an amount of from 1 milligram to 1 gram of compound per liter of solution.

14. In a high temperature rapid processing developing process comprising developing an exposed multi-layer silver halide color photographic material at a temperature of greater than 30° C., the improvement consisting of selectively inhibiting development of the uppermost photographic emulsion layer to improve the color balance and image quality of the developed color photographic material by processing said color photographic material no later than development in a photographic solution containing from 1 milligram to 1 gram per liter of solution of an effective development inhibitor for the uppermost photographic emulsion layer consisting essentially of a compound selected from the group consisting of

1,3,3a,7-tetraazaindene-4-thiol,
6-methyl-1,3,3a,7-tetraazaindene-4-thiol,
6-tertiary-butyl-1,3,3a,7-teraazaindene-4-thiol,
6-pentyl-1,3,3a,7-tetraazaindene-4-thiol,

6-nonyl-1,3,3a,7-tetraazaindene-4-thiol,
6-undecyl-1,3,3a,7-tetraazaindene-4-thiol,
6-heptadecyl-1,3,3a,7-tetraazaindene-4-thiol,
6-phenyl-1,3,3a,7-tetraazaindene-4-thiol,
5-bromo-6-methyl-1,3,3a,7-tetraazaindene-4-thiol,
2,6-dimethyl-1,3,3a,7-tetraazaindene-4-thiol,
5-ethyl-6-methyl-1,3,3a,7-tetraazaindene-4-thiol, and
5-iso-butyl-6-methyl-1,3,3a,7-tetraazaindene-4-thiol.

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