United States Patent [19]

Shimamura et al.

[11] **3,870,520**

[45] **Mar. 11, 1975**

[54] **PHOTOGRAPHIC PROCESSING COMPOSITION**

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[21] Appl. No.: **403,293**

[30] **Foreign Application Priority Data**

Oct. 5, 1972 Japan 47-100081

[52] **U.S. Cl.** .... **96/60 R,** 96/60 BF, 96/22

[51] **Int. Cl.** **G03c 5/32,** G03c 7/16

[58] **Field of Search** .... 96/60, 60 BF, 22, 53

[56] **References Cited**

UNITED STATES PATENTS

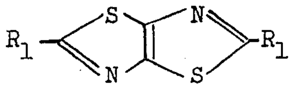
3,748,136 7/1973 Willems .... 96/60 R

Primary Examiner—Mary F. Kelley

Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & MacPeak

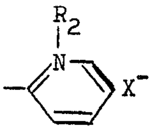
[57] **ABSTRACT**

A photographic processing composition, which comprises (1) a ferric ion complex or a persulfate and (2) a compound represented by the following general formula (I)



(I)

in which R_1 is



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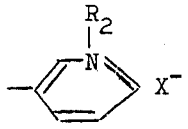

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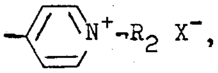


R_2 is an alkyl group or a $-(CH_2)-_n SO_3^-$ group, n is 3 or 4, and X^- is an anion, and being absent when R_2 is a $-(CH_2)- SO_3^-$ group.

27 Claims, No Drawings

PHOTOGRAPHIC PROCESSING COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a composition for photograhic processings and more particularly, it is concerned with an improved composition for bleaching and fixing.

2. Description of the Prior Art

In general, the basic processings of a silver halide color photographic light-sensitive material are color development and desilvering. That is to say, in an exposed silver halide color photographic material, the silver halide is reduced with a color developing agent to form silver in the color development step and the oxidation product of the color developing agent reacts with a color coupler to give a dye image. Thereafter, the color photographic material is subjected to the desilvering step, where the silver formed in the preceding step is oxidized with an oxidizing agent which is called a "bleaching agent" and then dissolved using a complexing agent which is called a "fixing agent". Thus, the silver is removed from the photographic material and only the dye image remains thereon. Development which is generally practiced, in addition to the above mentioned basic two steps of the color development and desilvering, involves auxiliary processing steps in order to retain the photographic and physical properties of the image as well as to improve the storage properties of an image. For example, these auxiliary processings are carried out using a hardening bath to prevent the light-sensitive layer(s) during processing from softening excessively, a stopping bath to stop the developing reaction effectively, an image stabilizing bath to stabilize the image and a film removing bath to remove the support backing layer.

Moreover, the above described desilvering step can be conducted either in one step using a bleaching and fixing bath wherein a bleaching agent and fixing agent are present in combination or in two steps using a bleaching bath and fixing bath separated.

As the bleaching solution, potassium ferricyanide is generally used. However, the bleaching solution using potassium ferricyanide has the disadvantages that a fatigued bleaching solution must be exchanged and the ferricyanide ion and the ferrocyanide ion in reduced form, which are discharged as an overflow during processing and as an entrainment in the washing water after bleaching, are subject to photochemical oxidation to thus form extremely toxic cyanide compounds. Therefore, it has been desired to develop a new bleaching agent which can be used in place of the potassium ferricyanide.

On the contrary, potassium bichromate, ferric ion complex salts, persulfates, quinones and copper salts have hitherto been used as a bleaching agent in addition to the potassium ferricyanide, but they are inferior in the oxidizing capacity and in ease of handling.

Ferric ion complex salts are used as a bleaching agent for a bleaching and fixing solution for color printing papers (German Pat. Nos. 866,605 and 966,410, and British Pat. Nos. 746,567, 933,088 and 1,014,396), but are not often used for color light-sensitive materials for photography, using silver iodobromide in a high concentration, since a bleaching and fixing agent containing a ferric ion complex salt has a low oxidizing capacity. Accordingly it is desirable to increase the oxidizing capacity of a bleaching and fixing solution or bleaching solution using a ferric ion complex salt.

Furthermore, ferric ion complex salts can be used as a bleaching agent with bromides. However, the disadvantage of a ferric ion complex salt bleaching bath is that a long time is required for bleaching because of a low bleaching capacity. Persulfates are known as bleaching agents in addition to the ferric ion complex salts. Ordinarily persulfates are used with bromides in a bleaching bath, but the disadvantage of a persulfate bleaching bath is that a much longer time is necessary for bleaching because of a lower bleaching capacity than that of the ferric ion complex salts.

As described above, a bleaching solution or bleaching and fixing solution using a ferric ion complex salt or a persulfate is not often used in color films using a high silver halide level and having a sensitivity sufficient for use in a camera, because of its weak bleaching capacity.

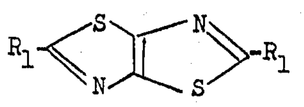
Therefore, it is an object of the invention to provide a photographic processing composition which has an accelerated bleaching action but which does not adversely affect the photographic characteristics.

It is another object of the invention to increase the bleaching capacity of a bleaching solution or bleaching and fixing solution containing a ferric ion complex salt or a persulfate.

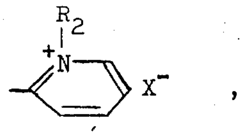
It is a further object of the invention to provide a method of rapidly bleaching or bleaching and fixing a color photographic material having a photographic sensitivity.

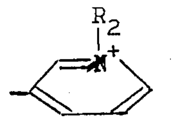
SUMMARY OF THE INVENTION

We, the inventors, have found as a result of our various studies that the above described objects can be accomplished with a photographic processing composition comprising a ferric ion complex salt or a persulfate and a compound represented by the following general formula,



in which R_1 is





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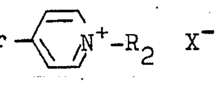


R_2 is an alkyl group (e.g., an alkyl group having from 1 to 5 carbon atoms) or $-(CH_2)_nSO^-_3$, n is 3 or 4 and X^- is an anion (e.g., a sulfonate ion or halide ion such as Cl^-, Br^-, or I^-), with X^- being absent when R_2 is $-(CH_2)_nSO_3^-$.

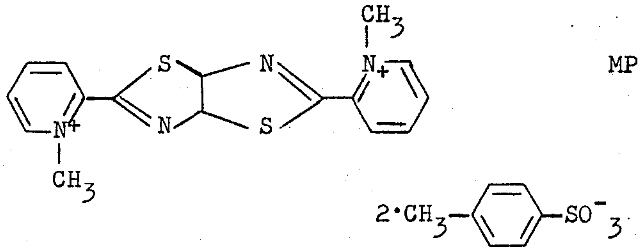
DETAILED DESCRIPTION OF THE INVENTION

The ferric ion complex salt or persulfate used in the invention acts as a bleaching agent of silver image as is well known in the art. One embodiment of the photographic processing composition according to the invention comprises at least one of the ferric ion complex salt and the persulfate and the above described compound, while another embodiment of the invention comprises compound and at least one of the ferric ion complex salt and the persulfate the above described compound and in addition a fixing agent. Compounds of the above general formula in which R_1 is as described above, R_2 is methyl, ethyl, $-(CH_2)_3SO_3^-$ or $-(CH_2)_4SO_3^-$ and in which X is a bromide ion or a p-toluene sulfonate ion are preferred.

Each component of the composition according to the invention will now be illustrated in detail.

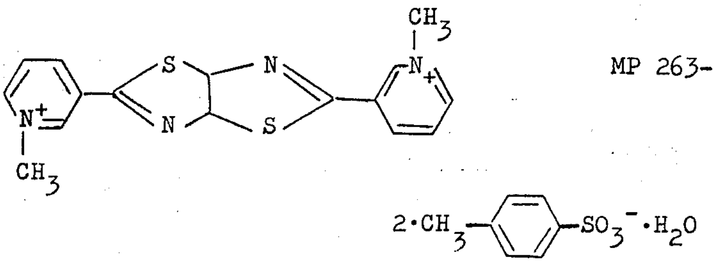
Specific examples of the compounds of the invention represented by the above described general formula are given as follows, but the invention is not to be interpreted as being limited to these compounds.

Compound 1



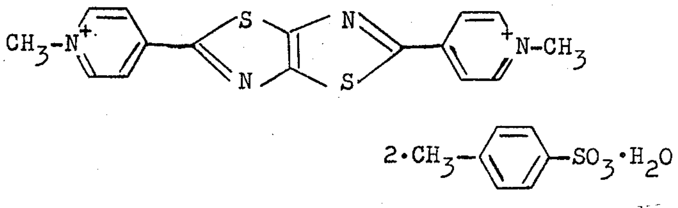
MP 260°C

Compound 2



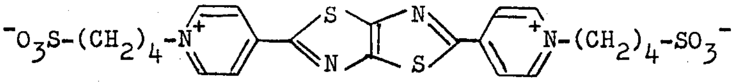
MP 263-265°C

Compound 3



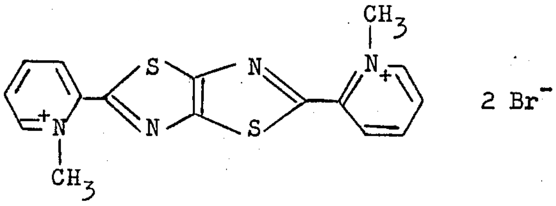
MP 282°C

Compound 4



MP>300°C

Compound 5



The general method of synthesizing the compound represented by the general formula as follows:

Equimolar amounts of rubeanic acid and pyridine aldehyde are heated with refluxing for 3 hours in dimethylformamide and the resulting crystal is quaternized with a corresponding reagent to obtain the desired compound.

The ferric ion complex used in the present invention is a complex of ferric ion with a chelating agent such as the aminopolycarboxylic acids, and the aminopolyphosphonic acids and their salts. The salts of the aminopolycarboxylic acids and the aminopolyphosphonic acids are the alkali metal, ammonium and water-soluble amine salts. Suitable alkali metal salts are the sodium, potassium and lithium salts and suitable water-soluble amine salts are salts of aliphatic amines such as methylamine, diethylamine, triethylamine and butylamine, alicyclic amines such as cyclohexylamine, aromatic amines such as aniline and m-toluidine, and heterocyclic amines such as pyridine, morpholine and piperidine.

Examples of suitable aminopolycarboxylic acids, aminopolyphosphonic acids and their salts which can be used as the chelating agents in this invention are

Ethylenediaminetetraacetic Acid
Disodium Ethylenediaminetetraacetate
Diammonium Ethylenediaminetetraacetate
Tetra(trimethylammonium) Ethylenediaminetetraacetate
Tetrapotassium Ethylenediaminetetraacetate
Tetrasodium Ethylenediaminetetraacetate
Trisodium Ethylenediaminetetraacetate
Diethylenetriaminepentaacetic Acid
Pentasodium Diethylenetriaminepentaacetate
Ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetic Acid
Trisodium Ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate
Triammonium Ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate
Propylenediaminetetraacetic Acid
Disodium Propylenediaminetetraacetate
Nitrilotriacetic Acid
Trisodium Nitrilotriacetate
Cyclohexanediaminetetraacetic Acid
Disodium Cyclohexanediaminetetraacetate
Iminodiacetic Acid
Dihydroxyethylglycine
Ethyletherdiaminetetraacetic Acid
Glycoletherdiaminetetraacetic Acid
Ethylenediaminetetrapropionic Acid
Phenylenediaminetetraacetic Acid
1,3-Diaminopropanol-N,N,N',N'-tetramethylenephosphonic Acid
Ethylenediamine-N,N,N'-tetramethylenephosphonic Acid
1,3-Propylenediamine-N,N,N',N'-tetramethylenephosphonic Acid

These compounds are given as typical examples and the present invention is not intended to be limited thereby.

The ferric ion complex salt can be used in the form of a complex salt or can be formed in solution using a ferric salt, for example, ferric sulfate, ferric chloride, ferric nitrate, ferric ammonium sulfate or ferric phosphate and a chelating agent, such as aminopolycarboxylic acid and an aminopolyphosphonic acid. Where a complex salt is employed, the complex salt can be used alone or a combination of two or more complex salts can be used. Where the complex salt is formed in solution from a ferric salt and a chelating agent, one or more ferric salts can be used and one or more chelating agents can be used. In either of these cases, the chelating agent can be used in excess for forming the ferric ion complex salt. The ferric ion complex salts are well known in the art, and described for example, in U.S. Pat. No. 3,582,322.

The persulfate used as a bleaching agent in the invention can be an alkali metal persulfate, such as potassium persulfate or sodium persulfate, or ammonium persulfate.

When the composition of the invention is used as a bleaching solution, a bromide, for example, an alkali metal bromide such as potassium bromide, sodium bromide, or an ammonium bromide can be contained therein in addition to the ferric ion complex salt and the compound of the invention described above. Furthermore, one or more inorganic acids, organic acids or their salts having a pH buffering function, for example, boric acid, borax, sodium metaborate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphoric acid, sodium phosphate, citric acid, sodium citrate and tartaric acid can be present.

Per 1000 ml of a bleaching solution, generally the quantity of the ferric ion complex salt or the persulfate is about 0.1 to 2 mols and that of the compound represented by the foregoing general formula is about 2×10^{-6} to 2×10^{-2}, preferably 1×10^{-4} to 1×10^{-2} mols. The pH of a bleaching solution during use generally is 3.0 to 8.0, preferably 4.0 to 7.0 in the case of a ferric ion complex salt and 1.0 to 7.0, preferably 2.0 to 6.0, in the case of a persulfate.

When the composition of the invention is used as a bleaching and fixing agent, on the other hand, one or more fixing agents can be used. Suitable examples of these fixing agents are thiosulfates such as sodium thiosulfate, ammonium thiosulfate, ammonium sodium thiosulfate and potassium thiosulfate, thiocyanates such as sodium thiocyanate, ammonium thiocyanate and potassium thiocyanate, and thioether compounds such as ethylenebisthioglycolic acid and 3,6-dithia-1,8-octanediol.

Per 1000 ml of a bleaching and fixing solution, the general quantity of the ferric ion complex salt or the persulfate is about 0.1 to 2 mols, that of the fixing agent is about 0.2 to 4 mols and that of the compound represented by the foregoing general formula is about 2×10^{-6} to 2×10^{-2} mol, preferably 1×10^{-4} to 1×10^{-2} mol.

To such bleaching and fixing solution can be added the above described additives which are disclosed as being suitable for addition to the bleaching solution, and sulfites such as the alkali metal sulfites, e.g., sodium sulfite, potassium sulfite, and ammonium sulfite. To the bleaching and fixing solution further can be added one or more compounds capable of accelerating the bleaching and fixing actions, for example, the polyamine compounds disclosed in Japanese Patent Publication Sho-45-8836, the thiourea derivatives disclosed in Japanese Patent Publication Sho-45-8506, the iodides described in German Pat. No. 1,127,715, the polyethylene oxides described in German Pat. No.

966,410, the nitrogen-containing heterocyclic compounds described in German Pat. No. 1,290,812 and other thioureas. The pH of the bleaching and fixing solutiong during use is usually 4.0 to 8.0, preferably 5.0 to 7.0.

The above described bleaching agent composition of this invention can be used for preparing a bleaching solution for use or as a solution to be used for replentishment and the above described bleaching and fixing agent composition can be used for preparing a bleaching and fixing solution for use or as a solution for replentishment. By the addition of the compound of the invention, the bleaching capacity can be increased and the ferric ion complex salt can be dissolved in a high concentration, thus giving an excellent bleaching agent or bleaching and fixing agent composition. In the case of the preparation of two or more solutions, therefore, the pH of the ferric ion complex salt-containing agent can be further increased outside of the above mentioned pH range. The components above described for preparing the bleaching or bleaching and fixing solutions can be combined ahead of time into a composition for subsequent use or can be added individually at the time of use.

The present invention can be suitably used and adapted to any of the processings for all types of color photographic materials using silver halide, for example, color papers, color negative films, color reversal films and color positive films as disclosed in U.S. Pat. No. 3,582,322.

The photographic processing composition containing the compound represented by the foregoing general formula has a strong bleaching capacity and can bleach silver in a short time. This bleaching period of time generally is shorter than 2 minutes although this time is varied depending on the temperature, processing conditions etc., employed. Moreover, a ferric ion complex can be contained therein and is not precipitated even at a low temperature, e.g., less than 10°C. In particular, the bleaching and fixing agent composition according to the invention is superior to bleaching and fixing agent compositions of the prior art in that with the bleaching and fixing agent composition of the invention, it is possible to bleach and fix well color photographic materials having a sensitivity sufficient for camera speed, for example, color negative films and color reversal films, where as it is difficult to bleach and fix such materials with prior art compositions.

The following examples are given in order to illustrate the invention in greater detail without intending to limit the same. Unless otherwise indicated all percents and parts are by weight.

EXAMPLE 1

This example was carried out using a color negative photographic material obtained by mixing and emulsifying a red-sensitive silver iodobromide emulsion (silver iodide 7 mol %) and 1-hydroxy-4-chloro-2-n-dodecylnaphthoamide as a cyan coupler, mixing and emulsifying a green-sensitive silver iodobromide (silver iodide 6 mol %) and 1-(2',4',6'-trichlorophenyl)-3-(3''-(2''', 4'''-di-t-amylphenoxyacetamide)benzamide)-5-pyrazolone as a magenta coupler and mixing and emulsifying a blue-sensitive silver iodobromide emulsion (silver iodide 6 mol %) and α-(2-methylbenzoyl)-aceto-(2'-chloro-5'-dodecoxycarbonyl)anilide as a yellow coupler, and then applying the resulting emulsions to a triacetate film base. For the emulsification of the each coupler, dibutyl phthalate and tricresyl phosphate were used as a coupler solvent, sorbitan monolaurate and sodium dodecylbenzenesulfonate were used as an emulsifier, and sodium 1-(p-nonylphenoxytrioxyethylene)butane-4-sulfonate and the lauric acid ester of sucrose were added as a coating aid.

This film was exposed and then subjected to the following processing I:

Processing I	
Color Development	12 min
Stopping Bath	4 do.
Hardening Bath	4 do.
Water Washing	4 do.
Bleaching and Fixing Bath	shown in the following table
Water Washing	8 do.
Drying	
Composition of Color Developer	
Benzyl Alcohol	5 ml
Sodium Hydroxide	0.5 g
Diethylene Glycol	3 ml
Sodium Hexametaphosphate	2 g
Sodium Sulfite	2 g
Potassium Bromide	2 g
4-Amino-3-methyl-N-ethyl-β-hydroxyethylaniline Sesquisulfate Monohydrate	5 g
Metaboric Acid	0.5 g
Sodium Metaborate	77 g
Water to	1000 ml
Stopping Solution	
Sodium Acetate	30 g
Glacial Acetic Acid	8 ml
Water to	1000 ml
Hardening Bath	
Sodium Hexametaphosphate	1 g
Borax Pentahydrate	20 g
Formalin (37%)	10 ml
Bleaching and Fixing Solution A	
Ferric Sodium Ethylenediaminetetraacetate (dihydrate)	80 g
Disodium Ethylenediaminetetraacetate (dihydrate)	15 g
Sodium Carbonate Monohydrate	17 g
Boric Acid	5 g
Sodium Sulfite	5 g
Ammonium Thiosulfate (70% aqueous solution)	160 ml
pH	5.5
Water to	1000 ml

Bleaching and Fixing Solution B

2×10^{-3} mol/liter of Compound 1 of the invention was added to Bleaching and Fixing Solution A.

Bleaching and Fixing Solution C

2×10^{-3} mol/liter of Compound 2 of the invention was added to Bleaching and Fixing Solution A.

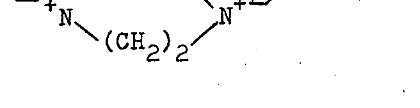
Bleaching and Fixing Solution D

2×10^{-3} mol/liter of Compound 3 of the invention was added to Bleaching and Fixing Solution A.

Bleaching and Fixing Solution E

2×10^{-3} mol/liter of a known compound* was added to Bleaching and Fixing Solution A.

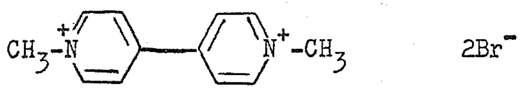
Compound*



Bleaching and Fixing Solution F

2×10^{-3} mol/liter of a known compound** was added to Bleaching and Fixing Solution A.

Compound **



The time for bleaching and fixing was determined by measuring the time required for complete desilvering as determined using X-ray fluorescent analysis. The results obtained are tabulated below:

Bleaching and Fixing Solution	Time for Bleaching and Fixing
A	4 min 20 sec
B	1 min 10 sec
C	1 min 40 sec
D	1 min 20 sec
E	3 min 20 sec
F	2 min 50 sec

The time required for bleaching and fixing was shortened when using Bleaching and Fixing Solutions B, C and D of the invention in comparison with the time required for Bleaching and Fixing Solutions A, E and F.

EXAMPLE 2

A color paper was prepared by applying to a sheet of baryta paper a silver bromide emulsion containing an emulsified yellow coupler dispersion, a silver chlorobromide emulsion containing an emulsified magenta coupler dispersion (silver chloride 70 mol %), a silver chlorobromide emulsion containing an emulsified cyan coupler dispersion (silver chloride 70 mol %) and a gelatin layer containing an ultraviolet light absorbent. Each coupler emulsion was prepared by dissolving the coupler in a mixture of dibutyl phthalate and tricresyl phosphate and dispersing in a gelatin solution an o/w type using sorbitan monolaurate, Turkey red oil and sodium dodecylbenzenesulfonate as an emulsifier. As the couplers, 1-(2', 4', 6'-trichlorophenyl)-3-(3''-(2''', 4'''-di-t-amylphenoxyacetamide)benzamide)-pyrazolone, 1-(hydroxy)-4-chloro-2-n-dodecylnaphthamide and α-(2-methylbenzoyl)-aceto-(2'-chloro-5'-dodecoxycarbonyl)anilide were used as the yellow, magenta and cyan couplers, respectively. As the ultra-violet absorbent, the one mentioned in Japanese Patent Publication Sho-45-9586 was used. As the emulsion hardener, the sodium salt of 2,4-dichloro-6-hydroxy-1,3,5-triazine was used. The thus prepared color paper was exposed using a color printer and then subjected to the following color development processings:

Development	Temperature	Time
Color Development	30°C	6 min
Stopping	do.	2 do.
Water Washing	do.	2 do.
Bleaching and Fixing	do.	shown in the following table
Water Washing	do.	2 do.
Stabilizing Bath	do.	2 do.
Drying	do.	2 do.

The processing solutions used had the following compositions:

Color Developer Composition	
Benzyl Alcohol	12 ml
Diethylene Glycol	3.5 ml
Sodium Hydroxide	20 g
Sodium Sulfite	2.0 g
Potassium Bromide	0.4 g
Sodium Chloride	1.0 g
Borax	4.0 g
Hydroxylamine Sulfate	2.0 g
Ethylenediaminetetraacetic Acid	2.0 g
4-Amino-3-methyl-N-ethyl-N-(β-sulfonamideethyl)aniline Sesquisulfate Monohydrate	5.0 g
Water to	1000 ml
Stopping Solution	
Sodium Thiosulfate	10 g
Ammonium Thiosulfate (70% aqueous solution)	30 ml
Sodium Acetate	5 g
Acetic Acid	30 ml
Potassium Alum	15 g
Water to	1000 ml
Stabilizing Solution	
Boric Acid	5 g
Sodium Citrate	5 g
Sodium Metaborate (tetrahydrate)	3 g
Potassium Alum	15 g
Water to	1000 ml
Bleaching and Fixing Solution G	
Ferric Sulfate	20 g
Disodium Ethylenediamine-tetraacetate Dihydrate	36 g
Sodium Carbonate Monohydrate	17 g
Sodium Sulfite	5 g
Ammonium Thiosulfate (70% aqueous solution)	100 ml
Boric Acid	5 g
pH	6.8
Water to	1000 ml

Bleaching and Fixing Solution H

1×10^{-3} mol/liter of Compound 3 of the invention was added to Bleaching and Fixing Solution G.

The time required for bleaching and fixing was measured using Bleaching and Fixing Solutions G and H. The results obtained are tabulated below:

Bleaching and Fixing Solution	Time for Bleaching and Fixing
G	60 sec
H	45 sec

The time required for bleaching and fixing was shortened when using Bleaching and Fixing Solution H of the invention in comparison with the time required using Bleaching and Fixing Solution G.

EXAMPLE 3

Two bleaching and fixing solutions having the following compositions were prepared:

Bleaching and Fixing Solution I	
Sodium Sulfite	5 g
Ferric Sodium Ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate	180 g
Sodium Thiocyanate	150 g
Sodium Thiosulfate (70% aqueous solution)	50 ml
Water to	1000 ml

Bleaching and Fixing Solution J

3×10^{-3} mol/liter of Compound 1 of the invention was added to Bleaching and Fixing Solution I.

The same color film as that described in Example 1 was used and subjected to the same processing as described in Example 1.

The time required for bleaching and fixing was measured using Bleaching and Fixing Solutions I and J. The results obtained are tabulated below:

Bleaching and Fixing Solution	Time for Bleaching and Fixing
I	1 min 30 sec
J	45 sec

The time required for bleaching and fixing was shortened when using Bleaching and Fixing Solution J of the invention in comparison with the time required using Bleaching and Fixing Solution I. The bleaching and fixing solution of the invention could also be used sufficiently as a bleaching and fixing solution for a commercially marketed internal-type reversal color film for example, as described in U.S. Pat. No. 3,582,322.

EXAMPLE 4

Processing I of Example 1 was carried out using a bleaching solution and fixing solution each having the following composition in place of the bleaching and fixing solution:

Bleaching Solution A	
Ferric Sodium Ethylenediaminetetraacetate Dihydrate	100 g
Potassium Bromide	50 g
pH	6.0
Water to	1000 ml

Bleaching Solution B

3×10^{-3} mol/liter of Compound 3 of the invention was added to Bleaching Solution A.

Fixing Solution	
Sodium Sulfite	4 g
Sodium Bisulfite	4 g
Ammonium Thiosulfate (70% aqueous solution)	140 ml
Water to	1000 ml

The time required for bleaching was measured using Bleaching Solutions A and B. Fixing was carried out for 6 minutes in any case. The results obtained are tabulated below:

Bleaching Solution	Time for Bleaching
A	3 min 10 sec
B	1 min

The time required for bleaching was shortened when using Bleaching Solution B of the invention in comparison with the time required when using Bleaching Solution A.

EXAMPLE 5

A similar procedure to that described in Example 4 was repeated but using bleaching solutions each having the following composition:

Bleaching Solution C	
Potassium Persulfate	50 g
Potassium Bromide	5 g
pH	3.2 g
Water to	1000 ml

Bleaching Solution D

5×10^{-3} mol/liter of Compound 1 of the invention was added to Bleaching Solution C.

The time required for bleaching was measured using Bleaching Solution C and D. The results obtained are tabulated below:

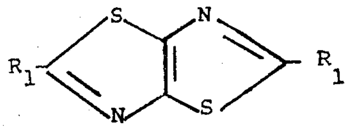
Bleaching Solution	Time for Bleaching
C	13 min
D	2 min 30 sec

The time required for bleaching was shortened when using Bleaching Solution D of the invention in comparison with the time required when using Bleaching Solution C.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

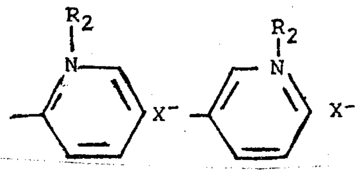
What is claimed is:

1. A photographic silver bleaching composition selected from the group consisting of a bleaching solution and a bleaching and fixing solution which comprises (1) a ferric ion complex or a persulfate and (2) a compound represented by the following general formula (I)

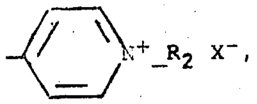


(I)

in which R_1 is



or



R_2 is an alkyl group or a $+CH_2+_nSO_3^-$ group; *n* is 3 or 4; and X^- is an anion, and being absent when R_2 is a $+CH_2+SO_3^-$ group.

2. The photographic processing composition as set forth in claim **1**, wherein R_2 is methyl, ethyl, $+CH_2+_3SO_3^-$ or $+CH_2+_4SO_3^-$, and wherein X^- is a bromide ion or a p-toluene sulfonate ion.

3. The photographic processing composition of claim **1**, wherein said composition is a bleaching solution.

4. The photographic processing composition of claim **3**, wherein said bleaching solution contains a bromide and a pH buffering agent.

5. The photographic processing composition composition of claim **4**, wherein said ferric ion complex salt or or said persulfate is present at about 0.1 to 2 mols per liter of said bleaching solution, wherein said compound of the general formula (I) is present at about 2×10^{-6} to 2×10^{-2} mols per liter of said bleaching solution and wherein the pH of said bleaching solution ranges from about 3 to 8 when said ferric ion complex is present and about 1 to 7 when said persulfate is present.

6. The photographic processing composition of claim **1**, wherein said compound of the general formula (I) is

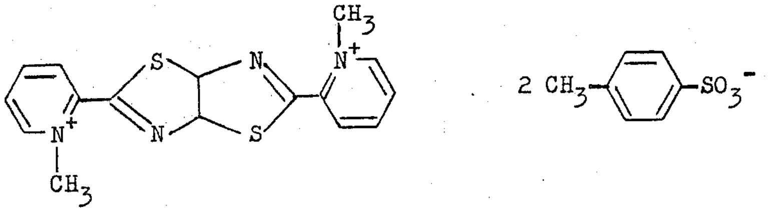
7. The photographic processing composition of claim **1**, wherein said composition is a bleaching and fixing solution.

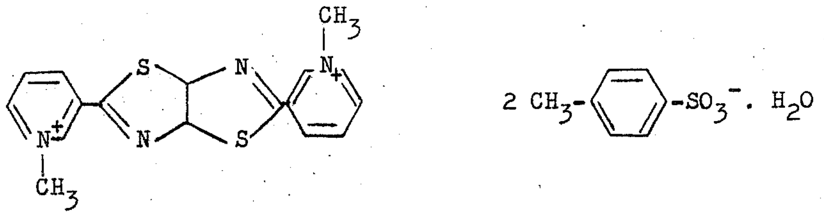
8. The photographic processing composition of claim **7**, wherein said solution contains a thiosulfate.

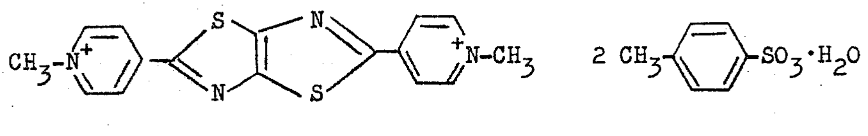
9. The photographic processing composition of claim **8**, wherein said ferric ion complex salt or said persulfate is present at about 0.1 to 2 mols per liter of said bleaching and fixing solution, wherein said fixing agent is present at about 0.2 to 4 mols per liter of said bleaching and fixing solution, wherein said compound of the general formula (I) is present at about 2×10^{-6} to 2×10^{-2} mols per liter of said bleaching and fixing solution, and wherein the pH of said bleaching and fixing solution is about 4 to 8.

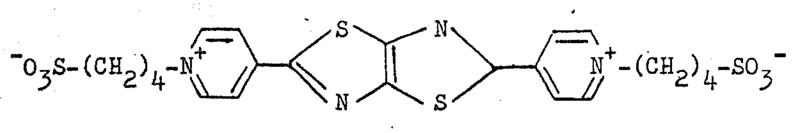
10. A method for development of an exposed light sensitive silver halide photographic element which comprises developing said silver halide photographic element and contacting said element with a bath containing the photographic processing composition of claim **1**.

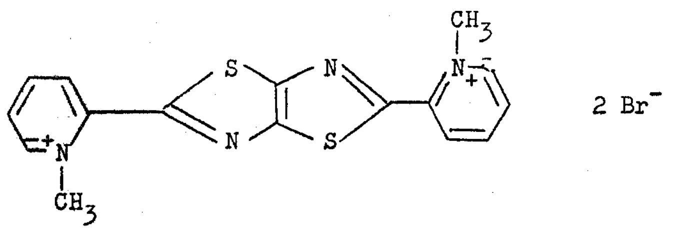
11. The method for development of claim **10**, wherein said composition is a bleaching solution.







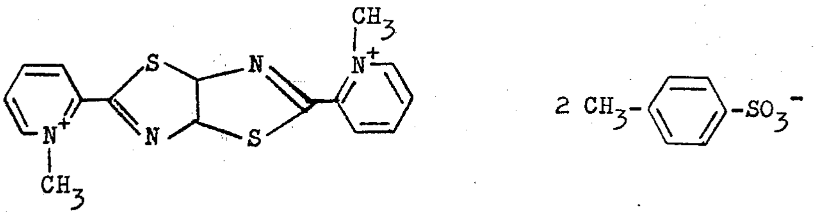


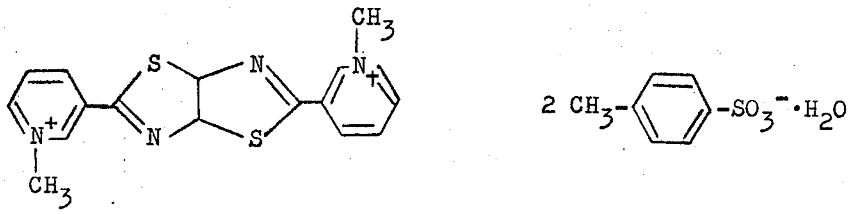


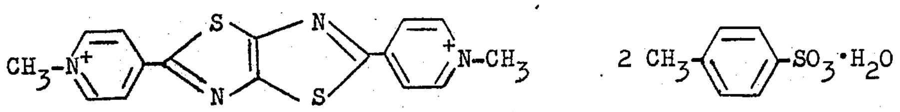
12. The method for development of claim **11,** wherein said bleaching solution contains additionally a bromide and a pH buffering agent.

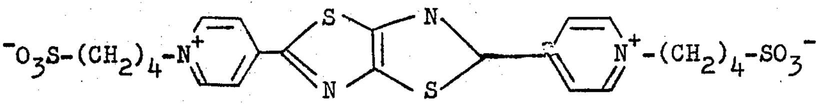
13. The method for development of claim **10,** wherein said compound of the general formula (I) is

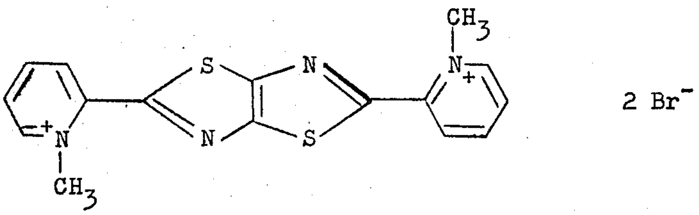
ide photographic element which comprises subjecting said silver halide photographic element to a silner bleaching or a silner bleaching and fixing with a bath containing the photographic processing composition of claim **1.**











14. The method of development of claim **10,** wherein said composition is a bleaching and fixing solution.

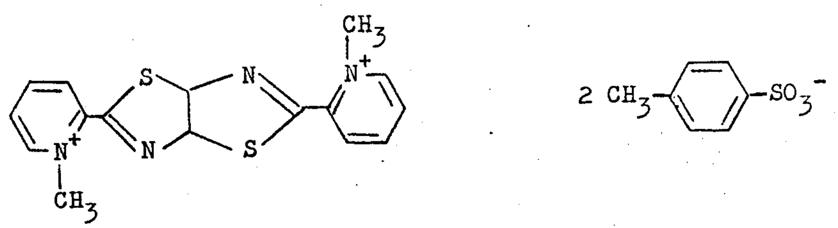
15. The method of development of claim **14,** wherein said solution contains a thiosulfate.

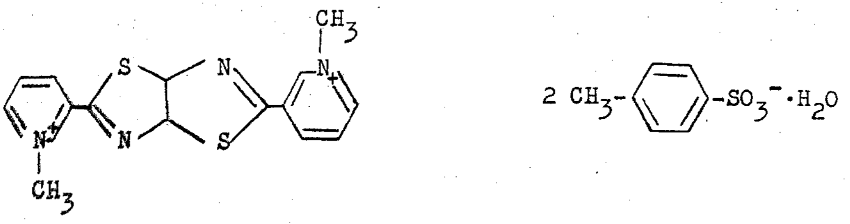
16. A method of accelerating the silner bleaching or the silner bleaching and fixing of a silver halide photographic element in the development of said silver halide photographic element ...

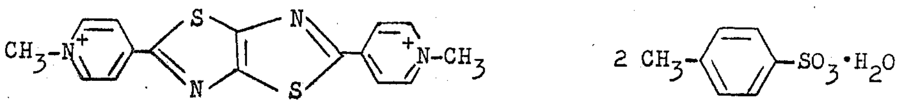
17. The method of accelerating of claim **16,** wherein said composition is a bleaching solution.

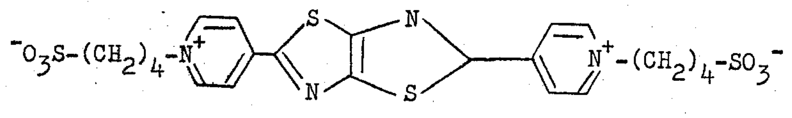
18. The method of accelerating of claim **17,** wherein said bleaching solution contains a bromide and a pH buffering agent.

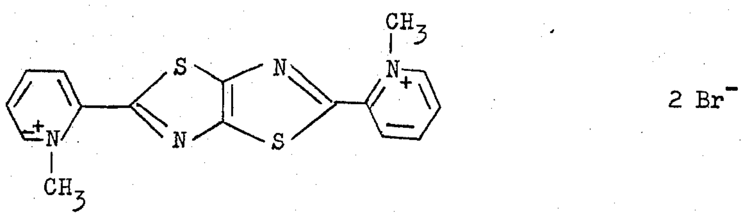
19. The method of accelerating of claim **16,** wherein said compound of the general formula (I) is











20. The method of accelerating of claim **16,** wherein said composition is a bleaching and fixing solution.

21. The method of accelerating of claim **20,** wherein said solution contains a thiosulfate.

22. The photographic processing composition of claim **1,** wherein said ferric ion complex salt is a complex with a member selected from the group consisting of an aminopolycarboxylic acid, an aminopolyphosphonic acid and their salts, which salts are selected from the group consisting of alkali metal, ammonium and water-soluble amine salts.

23. The method for development of claim **10,** wherein said ferric ion complex salt is a complex with a member selected from the group consisting of an aminopolycarboxylic acid, an aminopolyphosphonic acid and their salts, which salts are selected from the group consisting of alkali metal, ammonium and water-soluble amine salts.

24. The method of accelerating of claim **16,** wherein said ferric ion complex salt is a complex with a member selected from the group consisting of an aminopolycarboxylic acid, an aminopolyphosphonic acid and their salts, which salts are selected from the group consisting of alkali metal, ammonium and water-soluble amine salts.

25. The photographic processing composition of claim **1,** wherein said ferric ion complex is a complex with a member selected from the group consisting of an aminopolycarboxylic acid, and aminopolyphosphonic acid and their salts, which salts are selected from the group consisting of alkali metal, ammonium and water-soluble amine salts, wherein said acid is selected from the group consisting of ethylenediaminetetraacetic acid, disodium ethylenediaminetetraacetate, diammonium ethylenediaminetetraacetate, tetra(trimethylammonium) ethylenediaminetetraacetate, tetrapotassium ethylenediaminetetraacetate, tetrasodium ethylenediaminetetraacetate, trisodium ethylenediaminetetraacetate, diethylenetriaminepentaacetic acid, pentasodium diethylenetriaminepentaacetate, ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetic acid, trisodium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate, triammonium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate, propylenediaminetetraacetic acid, disodium propylenediaminetetraacetate, nitrilotriacetic acid, trisodium nitrilotriacetate, cyclohexandeiaminetetraacetic acid, disodium cyclohexanediaminetetraacetate, iminidiacetic acid, dihydroxyethylglycine, ethyletherdiaminetetraacetic acid, glycoletherdiaminetetraacetic acid, ethylenediaminetetrapropionic acid, phenylenediaminetetraacetic acid, 1,3-diaminopropanol-N,N,N',N'-tetramethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and 1,3-propylenediamine-N,N,N',N'-tetramethylenephosphonic acid.

26. The method for development of claim **10,** wherein said ferric ion complex is a complex with a member selected from the group consisting of an aminopolycarboxylic acid, an aminopolyphosphonic acid and their salts, which salts are selected from the group consisting of alkali metal, ammonium and water-soluble amine salts, wherein said acid is selected from the group consisting of ethylenediaminetetraacetic acid, disodium ethylenediaminetetraacetate, diammonium ethylenediaminetetraacetate, tetra(trimethylammonium) ethylenediaminetetraacetate, tetrapotassium ethylenediaminetetraacetate, tetrasodium ethylenediaminetetraacetate, trisodium ethylenediaminetetraacetate, diethylenetriaminepentaacetic acid, pentasodium diethylenetriaminepentaacetate, ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetic acid, trisodium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate, triammonium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate, propylenediaminetetraacetic acid, disodium propylenediaminetetraacetate, nitrilotriacetic acid, trisodium nitrilotriacetate, cyclohexanediaminetetraacetic acid, disodium cyclohexanediaminetetraacetate, iminodiacetic acid, dihydroxyethylglycine, ethyletherdiaminetetraacetic acid, glycoletherdiaminetetraacetic acid, ethylenediaminetetrapropionic acid, phenylenediaminetetraacetic acid, 1,3-diaminopropanol-N,N,N',N'-tetramethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and 1,3-propylenediamine-N,N,N',N'-tetramethylenephosphonic acid.

27. The method of accelerating of claim **16**, wherein said ferric ion complex is a complex with a member selected from the group consisting of an aminopolycarboxylic acid, an aminopolyphosphonic acid and their salts, which salts are selected from the group consisting of alkali metal, ammonium and water-soluble amine salts, wherein said acid is selected from the group consisting of ethylenediaminetetraacetic acid, disodium ethylenediaminetetraacetate, diammonium ethylenediaminetetraacetate, tetra(trimethylammonium) ethylenediaminetetraacetate, tetrapotassium ethylenediaminetetraacetate, tetrasodium ethylenediaminetetraacetate, trisodium ethylenediaminetetraacetate, diethylenetriaminepentaacetic acid, pentasodium diethylenetriaminepentaacetate, ethylenediamine-N-(β-oxyethyl)-N,N,N'-triacetic acid, trisodium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate, triammonium ethylenediamine-N-(β-oxyethyl)-N,N',N'-triacetate, propylenediaminetetraacetic acid, disodium propylenediaminetetraacetate, nitrilotriacetic acid, trisodium nitrilotriacetate, cyclohexanediaminetetraacetic acid, disodium cyclohexanediaminetetraacetate, iminodiacetic acid, dihydroxyethylglycine, ethyletherdiaminetetraacetic acid, glycoletherdiaminetetraacetic acid, ethylenediaminetetrapropionic acid, phenylenediaminetetraacetic acid, 1,3-diaminopropanol-N,N,N',N'-tetramethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and 1,3-propylenediamine-N,N,N',N'-tetramethylenephosphonic acid.

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