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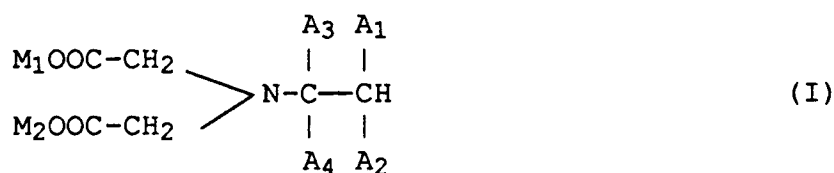
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W-8000 München 80 (DE)(54) **Bleach solution for colour photographic process.**

(57) Disclosed is a processing solution having bleachability for a light-sensitive silver halide color photographic material, which comprises at least a ferric complex salt of a compound represented by the following formula (I):



(wherein A₁, A₂, A₃ and A₄ may be the same or different, and each represent hydrogen atom, hydroxyl group, -COOM, -PO₃M₂, -CH₂OH or a lower alkyl group; at least one of A₁, A₂, A₃ and A₄ is -COOM or -PO₃M₂; M, M₁ and M₂ each represent hydrogen atom, ammonium group, sodium atom, potassium atom, lithium atom or an organic ammonium group),

which does not cause bleaching fog, enables rapid processing, has excellent biodegradability and environmental suitability, enables stable processing without causing sulfation, and prevents yellow stain at an edge portion of a light-sensitive material.

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BACKGROUND OF THE INVENTION

This invention relates to a processing solution having bleachability for a light-sensitive silver halide color photographic material, more specifically to a processing solution having bleachability for a light-sensitive silver halide color photographic material, which has excellent biodegradability, less bleaching fog and also excellent desilvering property.

In general, a light-sensitive silver halide color photographic material is processed by a color developing solution, a bleaching solution, a fixing solution, a bleach-fixing solution and a stabilizing solution. Among these processing solutions, a bleaching agent for bleaching silver is added to a bleaching solution and a bleach-fixing solution. At present, a bleaching agent used most generally for processing a color paper and a color negative film is a ferric complex salt of ethylenediaminetetraacetic acid. However, a ferric complex salt of ethylenediaminetetraacetic acid has poor biodegradability, and if it is flown out to rivers or soil, it will be accumulated without degradation or floated for a long time, which is undesirable from the standpoint of protection of environments of the earth. As a bleaching agent which has been used recently, there may be mentioned, for example, a ferric salt of 1,3-propanediaminetetraacetic acid (PDTA•Fe) disclosed in Japanese Provisional Patent Publications No. 103041/1990, No. 103040/1990 and No. 250651/1988. This PDTA•Fe is a compound having excellent silver bleachability, rapid processing suitability and also excellent biodegradability, but it has problems in practical use. That is, when bleaching processing is carried out immediately after color development, bleaching fog is caused. In order to solve this problem, there may be used a technique of lowering pH by using acetic acid, but this technique involves a problem of odor.

Another problem of the PDTA•Fe is that thiosulfate which is a fixing agent is decomposed and sulfurized because of strong oxidation power of the PDTA•Fe when processing is carried out by a fixing solution successively after a bleaching solution using the PDTA•Fe or when the PDTA•Fe is used as a bleaching agent of a bleach-fixing solution.

Further, as another bleaching agent, there has been known a ferric complex salt of diethylenetriaminepentaacetic acid disclosed in Japanese Provisional Patent Publications No. 118752/1986, No. 50145/1986, No. 50150/1986 and No. 50147/1986, but this bleaching agent also has a problem.

That is, when a color paper is processed by said bleaching agent, yellow stain is generated at an edge portion. This problem becomes serious and cannot be ignored particularly when low replenishing processing is carried out.

SUMMARY OF THE INVENTION

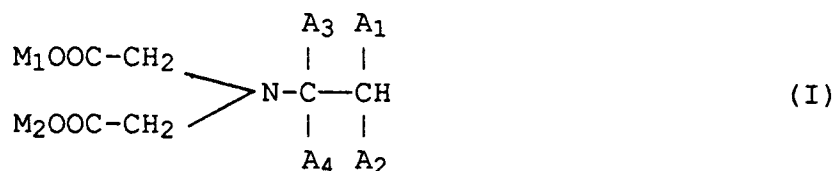
Thus, a first object of the present invention is to provide a processing solution having bleachability for a light-sensitive silver halide color photographic material, which does not cause bleaching fog and also enables rapid processing. A second object of the present invention is to provide a processing solution having bleachability for a light-sensitive silver halide color photographic material, which has excellent biodegradability and environmental suitability. Further, a third object of the present invention is to provide a processing solution having bleachability for a light-sensitive silver halide color photographic material, which enables stable processing without causing sulfurization. A fourth object of the present invention is to provide a processing solution having bleachability for a light-sensitive silver halide color photographic material, which prevents yellow stain at an edge portion of a light-sensitive material.

Other objects will be apparent in the following description.

The present inventors have studied intensively in order to solve the above problems, and consequently accomplished the present invention.

That is, the above objects of the present invention can be accomplished by the following processing solution (1), (2), (3), (4) or (5).

(1) A processing solution having bleachability for a light-sensitive silver halide color photographic material, which comprises at least a ferric complex salt of a compound represented by the following formula (I):



(wherein A_1 , A_2 , A_3 and A_4 may be the same or different, and each represent hydrogen atom, hydroxyl group, $-\text{COOM}$, $-\text{PO}_3\text{M}_2$, $-\text{CH}_2\text{OH}$ or a lower alkyl group; at least one of A_1 , A_2 , A_3 and A_4 is $-\text{COOM}$ or $-\text{PO}_3\text{M}_2$; M , M_1 and M_2 each represent hydrogen atom, ammonium group, sodium atom, potassium atom, lithium atom or an organic ammonium group).

(2) The processing solution having bleachability for a light-sensitive silver halide color photographic material described in the above (1) wherein the above processing solution is a bleaching solution.

(3) The processing solution having bleachability for a light-sensitive silver halide color photographic material described in the above (1) or (2) wherein the ratio of ammonium ion to whole cation in the above processing solution is 50 mole % or less.

(4) The processing solution having bleachability for a light-sensitive silver halide color photographic material described in the above (1), (2) or (3) wherein the above processing solution contains nitric acid or a nitrate.

(5) The processing solution having bleachability for a light-sensitive silver halide color photographic material described in the above (1), (2), (3) or (4) wherein the above processing solution contains a compound represented by the following formula (II):



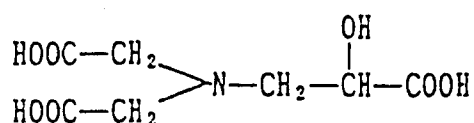
(wherein n represents an integer of 2 to 5; A represents a single bond or an n -valent organic group; M^1 represents hydrogen atom, an alkali metal atom or ammonium group; a plural number of M^1 's may be the same or different).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

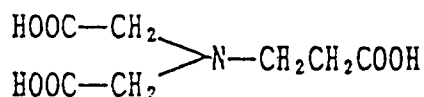
In the following, the present invention is explained in detail.

In the formula (I), A_1 , A_2 , A_3 and A_4 may be the same or different, and each represent hydrogen atom, hydroxyl group, $-\text{COOM}$, $-\text{PO}_3\text{M}_2$, $-\text{CH}_2\text{OH}$ or a lower alkyl group having 1 to 4 carbon atoms (methyl group, ethyl group, isopropyl group and n -propyl group). However, at least one of A_1 , A_2 , A_3 and A_4 is $-\text{COOM}$ or $-\text{PO}_3\text{M}_2$. M , M_1 and M_2 each represent hydrogen atom, ammonium group, sodium atom, potassium atom, lithium atom or an organic ammonium group (e.g. trimethylammonium group and triethanolammonium group).

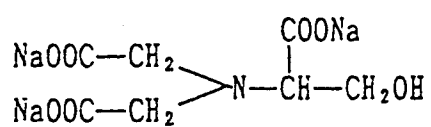
In the following, preferred specific examples of the compound represented by the formula (I) are shown.
(I-1)



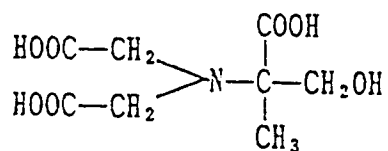
(I-2)



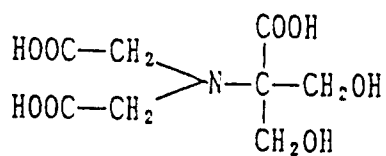
(I-3)



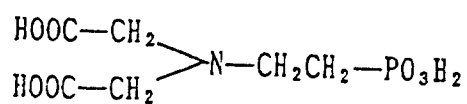
(I-4)



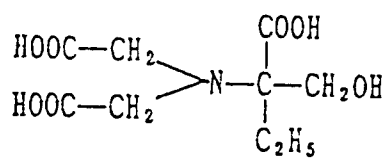
(I-5)



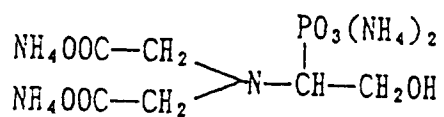
(I-6)



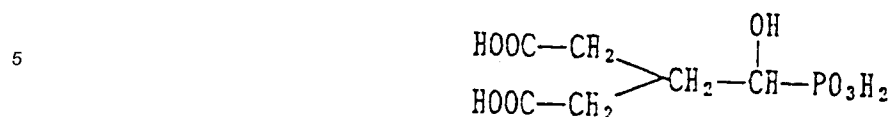
(I-7)



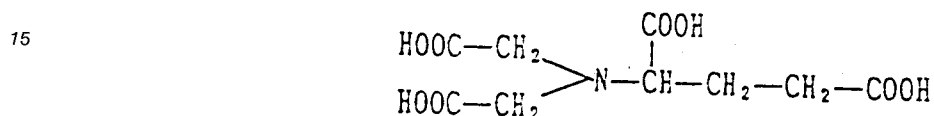
(I-8)



(I-9)



(I-10)



The above compounds represented by the formula (I) can be synthesized according to common synthetic methods disclosed in Japanese Provisional Patent Publications No. 267750/1988, No. 267751/1988, No. 115172/1990 and No. 295954/1990.

"The processing solution having bleachability" according to the present invention means specifically a bleaching solution, a bleach-fixing solution and a bleach-fixing solution for one bath development.

The amount of a ferric complex salt of the compound represented by the above formula (I) to be contained is preferably in the range of 0.1 to 2.0 mole, more preferably in the range of 0.15 to 1.5 mole per liter of the bleaching solution or bleach-fixing solution.

In the present invention, the bleaching solution or bleach-fixing solution may contain ferric complex salts of the following compounds other than a ferric complex salt of the compound represented by the above formula (I) as a bleaching agent.

- (A'-1) Ethylenediaminetetraacetic acid
- (A'-2) Trans-1,2-cyclohexanediaminetetraacetic acid
- (A'-3) Dihydroxyethylglycine
- (A'-4) Ethylenediaminetetrakis(methylenephosphonic) acid
- (A'-5) Nitrilotris(methylenephosphonic) acid
- (A'-6) Diethylenetriaminepenta(methylenephosphonic) acid
- (A'-7) Diethylenetriaminepentaacetic acid
- (A'-8) Ethylenediaminediortho(hydroxyphenyl)acetic acid
- (A'-9) Hydroxyethylethylenediaminetriacetic acid
- (A'-10) Ethylenediaminepropionic acid
- (A'-11) Ethylenediaminediacetic acid
- (A'-12) Hydroxyethyliminodiacetic acid
- (A'-13) Nitrilotriacetic acid
- (A'-14) Nitrilotripropionic acid
- (A'-15) Triethylenetetraminehexaacetic acid
- (A'-16) Ethylenediaminetetrapropionic acid
- (A'-17) 1,3-Propylenediaminetetraacetic acid
- (A'-18) Glycol ether diaminetetraacetic acid

In the present invention, an effect on rapid processing can be exhibited by incorporating at least one of imidazole or a derivative thereof disclosed in Japanese Provisional Patent Publication No. 295258/1989 or compounds represented by the formulae (I) to (IX) and exemplary compounds thereof disclosed in the same patent publication into the bleaching solution, bleach-fixing solution and fixing solution.

In addition to the above accelerators, exemplary compounds disclosed on pp. 51 to 115 of Japanese Provisional Patent Publication No. 123459/1987, exemplary compounds disclosed on pp. 22 to 25 of Japanese Provisional Patent Publication No. 17445/1988, and compounds disclosed in Japanese Provisional Patent Publications No. 95630/1978 and No. 28426/1978 may be also used.

The bleaching solution or bleach-fixing solution is preferably used at a temperature of 20 to 50 °C, desirably 25 to 45 °C.

The pH of the bleaching solution is preferably 6.0 or less, more preferably 1.0 to 5.5. The pH of the bleach-fixing solution is preferably 5.0 to 9.0, more preferably 6.0 to 8.5. The pH of the bleaching solution or bleach-fixing solution is a pH of a processing tank at the time of processing a light-sensitive silver halide material, which is clearly distinguished from a pH of a replenishing solution.

In the bleaching solution or bleach-fixing solution, in addition to those described above, a halide such as ammonium bromide, potassium bromide and sodium bromide, and various fluorescent brighteners, de-foaming agents or surfactants may be contained.

The replenishing amount of the bleaching solution or bleach-fixing solution is preferably 500 ml or less, more preferably 20 ml to 400 ml, most preferably 40 ml to 350 ml per 1 m² of a light-sensitive silver halide color photographic material. When a replenished amount is smaller, the effect of the present invention becomes remarkable.

In the present invention, in order to increase activity of the bleaching solution or bleach-fixing solution, air or oxygen may be blown into a processing bath or a tank for storing a processing replenishing solution if desired, or a suitable oxidizer, for example, hydrogen peroxide, hydrobromide and persulfate may be added.

As a fixing agent to be used in the fixing solution or bleach-fixing solution according to the present invention, thiocyanate and thiosulfate are preferably used. The amount of thiocyanate to be contained is preferably at least 0.1 mole/liter, and when a color negative film is processed, the amount is more preferably 0.5 mole/liter or more, particularly preferably 0.1 mole/liter or more. The amount of the thiosulfate to be contained is preferably at least 0.2 mole/liter, and when a color negative film is processed, the amount is more preferably 0.5 mole/liter or more.

In the present invention, the object of the present invention can be accomplished more effectively by using thiocyanate and thiosulfate in combination.

In the fixing solution or bleach-fixing solution according to the present invention, in addition to these fixing agents, a pH buffer comprising various salts may be contained alone or in combination of two or more. Further, a large amount of a rehalogenating agent such as an alkali halide or an ammonium halide, for example, potassium bromide, sodium bromide, sodium chloride and ammonium bromide is desirably contained.

Also, compounds which have been generally added to a fixing solution or bleach-fixing solution such as alkylamines and polyethylene oxides may be suitably added.

From the bleach-fixing solution according to the present invention, silver may be recovered by a known method.

To the fixing solution or bleach-fixing solution, a compound represented by the following formula (FA) and exemplary compounds thereof disclosed on p. 56 of Japanese Provisional Patent Publication No. 295258/1989 are preferably added not only for exhibiting the effect of the present invention more favorably, but also for exhibiting another effect that extremely less sludge is generated in a processing solution having fixing ability when a small quantity of light-sensitive materials are processed for a long time.



wherein R' and R'' each represent hydrogen atom, an alkyl group, an aryl group, an aralkyl group or a nitrogen-containing heterocyclic ring; and n' represents 2 or 3.

The compounds represented by the formula (FA) disclosed in Japanese Provisional Patent Publication No. 295258/1989 can be synthesized by a common method as disclosed in U.S. Patents No. 3,335,161 and No. 3,260,718. These compounds represented by the above formula (FA) may be used alone or in combination of two or more.

By adding these compounds represented by the formula (FA) in an amount of 0.1 to 200 g per liter of the processing solution, good results can be obtained.

The processing times with the bleaching solution and the fixing solution are optional, but each processing time is preferably 3 minutes 30 seconds or shorter, more preferably 10 seconds to 2 minutes 20

seconds, particularly preferably in the range of 20 seconds to 1 minute 20 seconds. The processing time with the bleach-fixing solution is preferably 4 minutes or shorter, more preferably in the range of 10 seconds to 2 minutes 20 seconds.

In practicing the present invention, when the ratio of ammonium ion to whole cation in the processing solution having bleachability of the present invention is 50 mole % or less, the effect of the present invention can be exhibited more favorably. Said ratio is more preferably 30 mole % or less, most preferably 10 mole % or less.

The nitrate according to the present invention includes specifically sodium nitrate, ammonium nitrate, potassium nitrate and lithium nitrate.

Next, the compound represented by the above formula (II) is described.

In the formula (II), as the n-valent organic group represented by A, there may be mentioned an alkylene group (e.g. methylene group, ethylene group, trimethylene group and tetramethylene group), an alkenylene group (e.g. ethenylene group), an alkynylene group (e.g. ethynylene group), a cycloalkylene group (e.g. 1,4-cyclohexanediyl), an arylene group (e.g. o-phenylene group and p-phenylene group), an alkanetriyl group (e.g. 1,2,3-propanetriyl group) and an allenetriyl group (e.g. 1,2,4-benzenetriyl group).

The n-valent group represented by A described above includes those having a substituent(s) (e.g. hydroxy group, an alkyl group and a halogen atom) such as 1,2-dihydroxyethylene, hydroxyethylene, 2-hydroxy-1,2,3-propanetriyl, methyl-p-phenylene, 1-hydroxy-2-chloroethylene, chloromethylene and chloroethylene.

In the following, preferred specific examples of the compound represented by the formula (II) are shown.

(II-1) $\text{HOOCCH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{COOH}$

(II-2) $\text{HOOC}(\text{CHOH})_2\text{COOH}$

(II-3) $\text{HOOCCH}_2\text{COOH}$

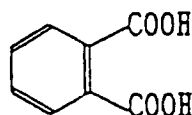
(II-4) $\text{HOOCCH}(\text{OH})\text{CH}_2\text{COOH}$

(II-5) $\text{HOOCCH}=\text{CHCOOH}$

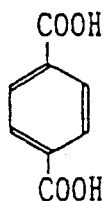
(II-6) $\text{HOOCCH}_2\text{CH}_2\text{COOH}$

(II-7) $(\text{COOH})_2$

(II-8)



(II-9)



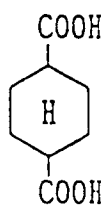
(II-10) $\text{NaOOCCH}=\text{CHCOONa}$

(II-11) $\text{KOOCCCH}=\text{CHCOOK}$

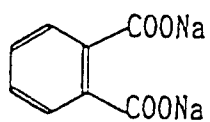
(II-12) $\text{H}_4\text{NOOCCH}=\text{CHCOONH}_4$

(II-13)

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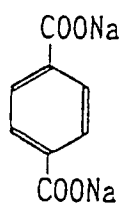
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(II-15)

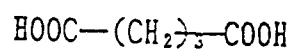
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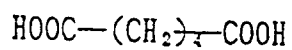
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(II-16)

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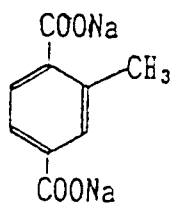
35 (II-17)



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(II-18) $\text{HOOC}\equiv\text{CCOOH}$ (II-19)

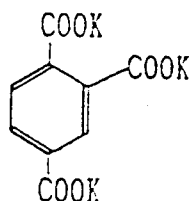
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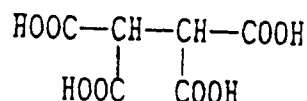
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(II-20)

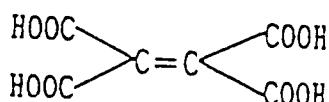
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(II-21)



(II-22)



Among the above exemplary compounds, particularly preferred are Exemplary compounds (II-1), (II-3), (II-4), (II-5), (II-16) and (II-18), and most preferred is Exemplary compound (II-5).

The compound represented by the formula (II) is preferably contained in an amount of 0.05 to 2.0 mole, more preferably 0.2 to 1.0 mole per liter of the processing solution having bleachability.

A buffer such as acetic acid may be used in combination within the range which does not impair the effect of the present invention. In the embodiment of the present invention, it is preferred that acetic acid is used in combination.

According to the investigation by the present inventors, the problem caused by using acetic acid described above relates closely to the amount of acetic acid and pH. Even if the pH is in the range of the present invention, when the amount of acetic acid used is 0.6 mole/liter or less, preferably 0.5 mole/liter or less, the above problem is permissible. Further, in the points of buffering property and cost, acetic acid is advantageously used in combination.

EXAMPLES

The present invention is described in detail by referring to Examples, but the present invention is not limited to these Examples.

Example 1

Preparation of light-sensitive color photographic material (color paper)

On a support having one surface on which polyethylene was laminated and the other surface on which polyethylene containing titanium oxide was laminated at a first layer side, the respective layers having the following constitutions were provided by coating to prepare a multilayer light-sensitive color photographic material. Coating solutions were prepared as described below.

First layer coating solution

In 6.67 g of a high boiling point solvent (DNP) were dissolved 26.7 g of a yellow coupler (Y-1), 100 g of a dye image stabilizer (ST-1), 6.67 g of a dye image stabilizer (ST-2) and 0.67 g of an additive (HQ-1) by adding 60 ml of ethyl acetate. The solution was emulsified and dispersed in 220 ml of a 10 % gelatin aqueous solution containing 7 ml of a 20 % surfactant (SU-1) by using an ultrasonic homogenizer to prepare a yellow coupler dispersion. The dispersion was mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared under the following conditions to prepare a first layer coating solution.

Second layer to seventh layer coating solutions were prepared in the same manner as the above first layer coating solution.

As a hardener, (H-1) was added to the second layer and fourth layer, and (H-2) was added to the seventh layer. As a coating aid, surfactants (SU-2) and (SU-3) were added for controlling surface tension.

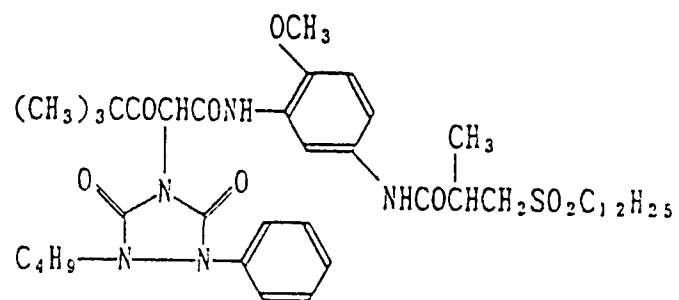
Table 1

Layer	Constitution	Amount added (g/m ²)
Seventh layer (Protective layer)	Gelatin	1.0
Sixth layer (UV absorbing layer)	Gelatin	0.35
	UV absorber (UV-1)	0.10
	UV absorber (UV-2)	0.04
	UV absorber (UV-3)	0.18
	Antistaining agent (HQ-1)	0.01
	DNP	0.18
	PVP	0.03
	Antiirradiation dye (AI-2)	0.02
Fifth layer (Red-sensitive layer)	Gelatin	1.21
	Red-sensitive silver chloro-bromide emulsion (EmC) (calculated on silver)	0.19
	Cyan coupler (C-1)	0.20
	Cyan coupler (C-2)	0.25
	Dye image stabilizer (ST-1)	0.20
	Antistaining agent (HQ-1)	0.01
	HBS-1	0.20
	DOP	0.20

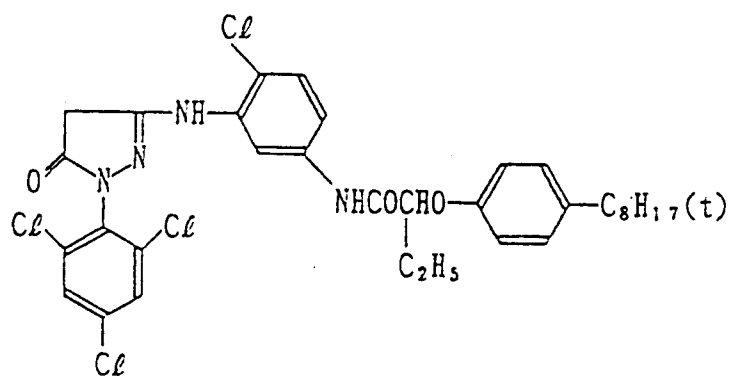
Table 1 (cont'd)

Layer	Constitution	Amount added (g/m ²)
Fourth layer (UV absorbing layer)	Gelatin	0.90
	UV absorber (UV-1)	0.28
	UV absorber (UV-2)	0.08
	UV absorber (UV-3)	0.38
	Antistaining agent (HQ-1)	0.03
	DNP	0.35
Third layer (Green-sensitive layer)	Gelatin	1.40
	Green-sensitive silver chlorobromide emulsion (EmB)	
	(calculated on silver)	0.15
	Magenta coupler (M-C)	0.32
	Dye image stabilizer (ST-3)	0.15
	Dye image stabilizer (ST-4)	0.15
	Dye image stabilizer (ST-5)	0.15
	DNP	0.20
	Antiirradiation dye (AI-1)	0.02
Second layer (Intermediate layer)	Gelatin	1.20
	Antistaining dye (HQ-2)	0.12
	DIDP	0.15
First layer (Blue-sensitive layer)	Gelatin	1.20
	Blue-sensitive silver chlorobromide emulsion (EmA)	
	(calculated on silver)	0.25
	Yellow coupler (Y-1)	0.82
	Dye image stabilizer (ST-1)	0.30
	Dye image stabilizer (ST-2)	0.20
	Antistaining agent (HQ-1)	0.02
	Antiirradiation dye (AI-3)	0.02
	DNP	0.20
Support	Polyethylene-laminated paper	

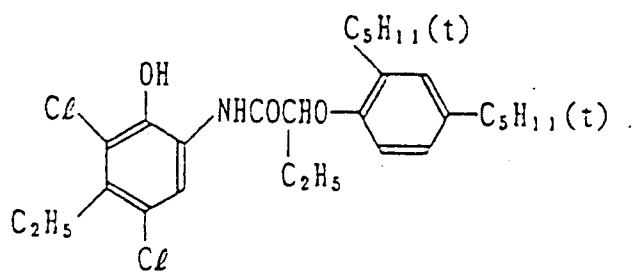
Y-1



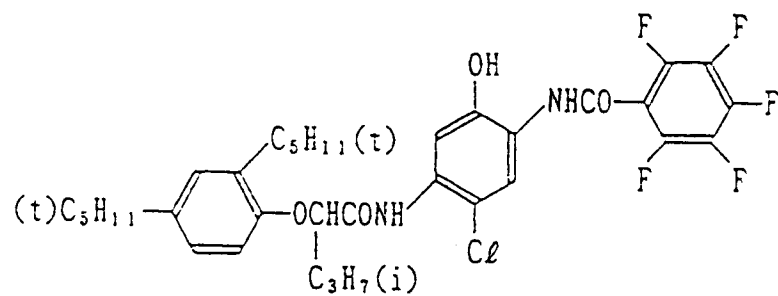
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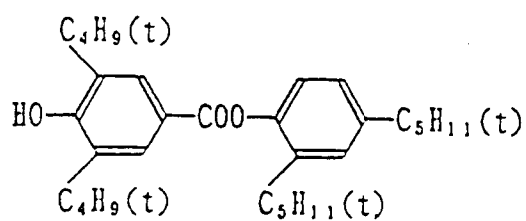
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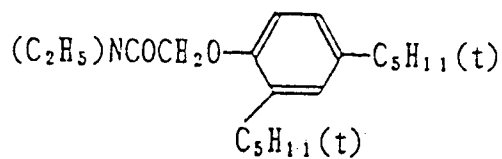
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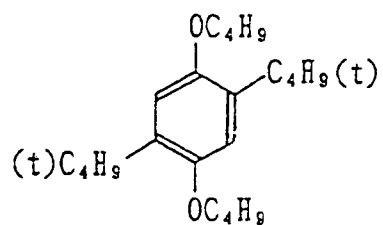
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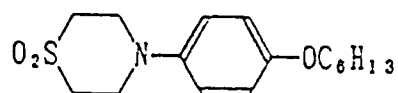
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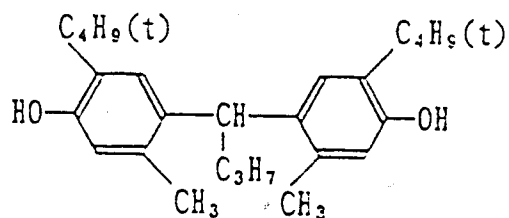
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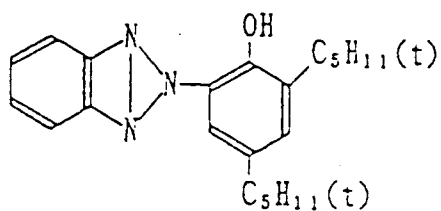
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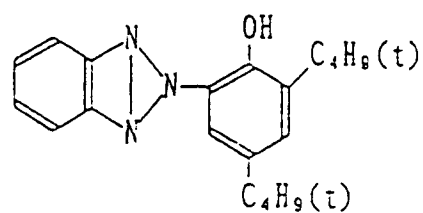
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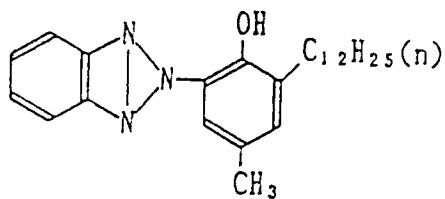
UV-1



UV-2

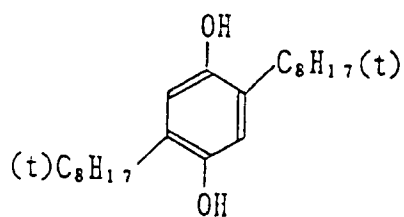


UV-3

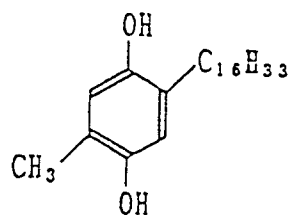


DOP Dioctyl phthalate
 DNP Dinonyl phthalate
 DIDP Diisodecyl phthalate
 PVP Polyvinyl pyrrolidone

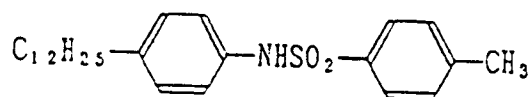
HQ-1



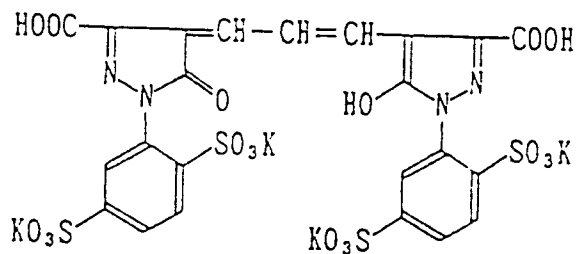
HQ-2



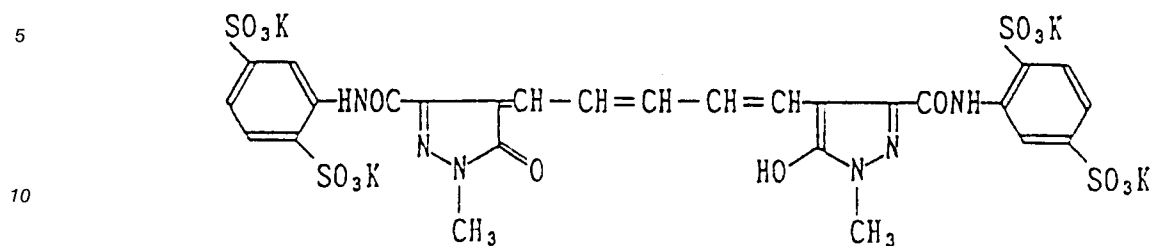
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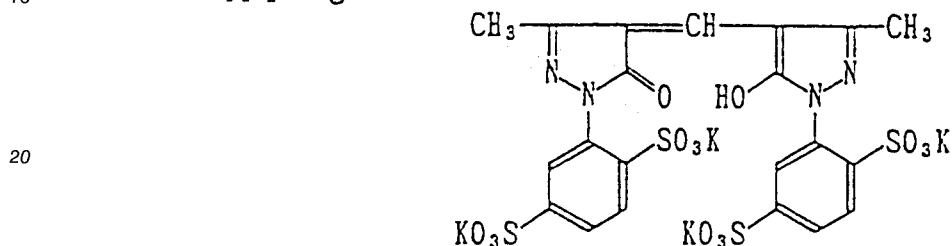
AI-1



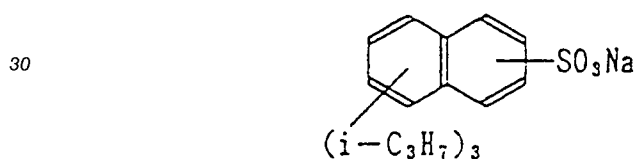
A I - 2



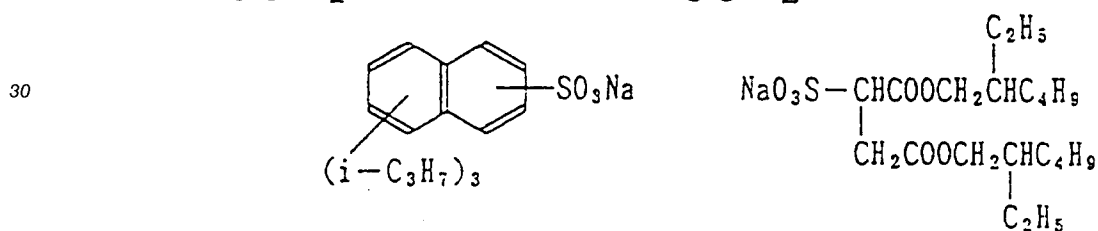
A I - 3



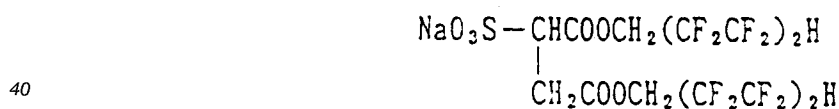
S U - 1



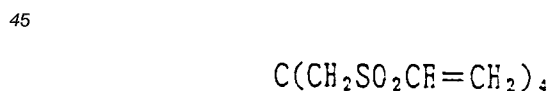
S U - 2



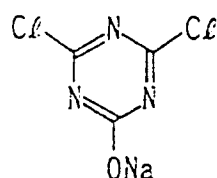
S U - 3



H - 1



H - 2



(Preparation method of blue-sensitive silver halide emulsion)

To 1000 ml of a 2 % gelatin aqueous solution maintained at 40 °C were added the following (Solution A) and (Solution B) simultaneously over 30 minutes while controlling pAg = 6.5 and pH = 3.0, and further added the following (Solution C) and (Solution D) simultaneously over 180 minutes while controlling pAg =

7.3 and pH = 5.5.

During the above addition, the pAg was controlled by the method disclosed in Japanese Provisional Patent Publication No. 45437/1984, and the pH was controlled by using an aqueous solution of sulfuric acid or sodium hydroxide.

(Solution A)	
Sodium chloride	3.42 g
Potassium bromide	0.03 g
made up to 200 ml with addition of water.	

(Solution B)	
Silver nitrate	10 g
made up to 200 ml with addition of water.	

(Solution C)	
Sodium chloride	102.7 g
Potassium bromide	1.0 g
made up to 600 ml with addition of water.	

(Solution D)	
Silver nitrate	300 g
made up to 600 ml with addition of water.	

After completion of the addition, desalting was carried out by using a 5 % aqueous solution of Demol N (trade name) produced by Kao Atlas Co. and a 20 % aqueous solution of magnesium sulfate, and then the mixture obtained was mixed with a gelatin aqueous solution to obtain a monodispersed cubic emulsion EMP-1 having an average grain size of 0.85 μm , a variation coefficient of a grain size distribution of 7 %, and a silver chloride content of 99.5 mole %.

The above emulsion EMP-1 was chemically ripened at 50 °C for 90 minutes by using the following compounds to obtain a blue-sensitive silver halide emulsion (Em-A).

Sodium thiosulfate	0.8 mg/mole of AgX
Chloroauric acid	0.5 mg/mole of AgX
Stabilizer (STAB-1)	6×10^{-4} mole/mole of AgX
Sensitizing dye (BS-1)	4×10^{-4} mole/mole of AgX
Sensitizing dye (BS-2)	1×10^{-4} mole/mole of AgX

(Preparation method of green-sensitive silver halide emulsion)

In the same manner as in EMP-1 except for changing addition time of (Solution A) and (Solution B) and addition time of (Solution C) and (Solution D), a monodispersed cubic emulsion EMP-2 having an average grain size of 0.43 μm , a variation coefficient of a grain size distribution of 8 %, and a silver chloride content of 99.5 mole % was prepared.

EMP-2 was chemically ripened by using the following compounds at 55 °C for 120 minutes to obtain a green-sensitive silver halide emulsion (Em-B)

Sodium thiosulfate	1.5 mg/mole of AgX
Chloroauric acid	1.0 mg/mole of AgX
Stabilizer (STAB-1)	6×10^{-4} mole/mole of AgX
Sensitizing dye (GS-1)	4×10^{-4} mole/mole of AgX

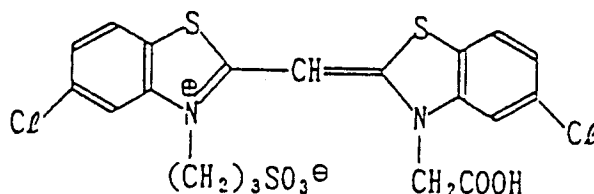
(Preparation method of red-sensitive silver halide emulsion)

In the same manner as in EMP-1 except for changing addition time of (Solution A) and (Solution B) and addition time of (Solution C) and (Solution D), a monodispersed cubic emulsion EMP-3 having an average grain size of $0.50 \mu\text{m}$, a variation coefficient of a grain size distribution of 8 %, and a silver chloride content of 99.5 mole % was prepared.

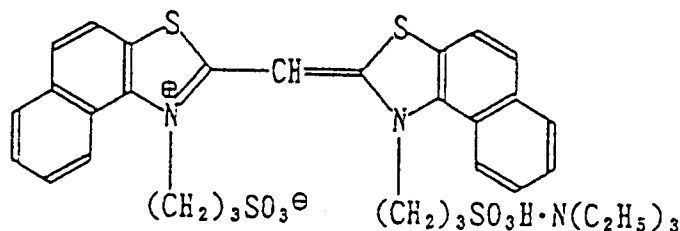
EMP-3 was chemically ripened by using the following compounds at 60°C for 90 minutes to obtain a red-sensitive silver halide emulsion (Em-C)

Sodium thiosulfate	1.8 mg/mole of AgX
Chloroauric acid	2.0 mg/mole of AgX
Stabilizer (STAB-1)	6×10^{-4} mole/mole of AgX
Sensitizing dye (RS-1)	4×10^{-4} mole/mole of AgX

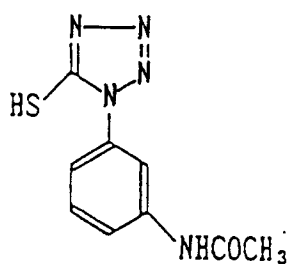
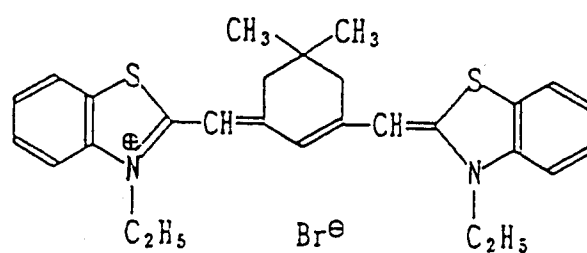
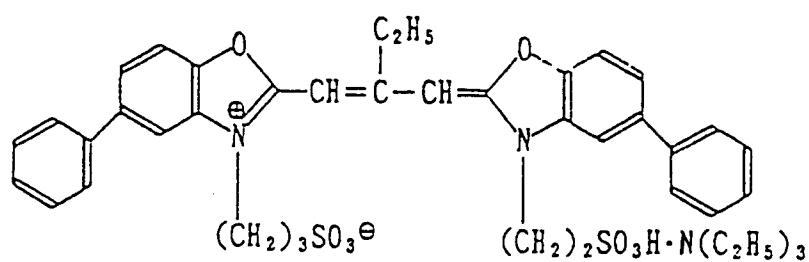
B S - 1



B S - 2



G S - 1



The above light-sensitive color photographic material (color paper) was exposed according to a conventional method, and processed by using the following processing steps and processing solutions.

40

Processing step	Processing temperature	Processing time	Amount replenished
(1) Color developing	35.0 ± 0.3 °C	45 sec	162 ml/m ²
(2) Bleach-fixing	35.0 ± 0.5 °C	45 sec	100 ml/m ²
(3) Stabilizing (3 tank cascade)	30 to 34 °C	90 sec	248 ml/m ²
(4) Drying	60 to 80 °C	30 sec	

45

Color developing solution		
5	Triethanolamine	10 g
	Diethylene glycol	6 g
	N,N-Diethylhydroxylamine	3.6 g
	Hydrazinodiacetic acid	5.0 g
	Potassium bromide	20 mg
10	Potassium chloride	3.5 g
	Diethylenetriaminepentaacetic acid	5 g
	Potassium sulfite	0.3 g
	Color developing agent (3-methyl-4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)aniline sulfate)	5.5 g
	Potassium carbonate	25 g
15	Potassium hydrogen carbonate	5 g
	made up to 1 liter in total with addition of water, and adjusted to pH 10.10 with potassium hydroxide or sulfuric acid.	

Color developing replenishing solution		
20	Triethanolamine	14.0 g
	Diethylene glycol	8.0 g
	N,N-diethylhydroxylamine	5 g
	Hydrazinodiacetic acid	7.5 g
25	Potassium bromide	2 mg
	Potassium chloride	2.5 g
	Diethylenetriaminepentaacetic acid	7.5 g
	Potassium sulfite	0.5 g
	Color developing agent (3-methyl-4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)aniline sulfate)	8 g
30	Potassium carbonate	30 g
	Potassium hydrogen carbonate	1 g
made up to 1 liter in total with addition of water, and adjusted to pH 10.40 with potassium hydroxide or sulfuric acid.		

Bleach-fixing solution		
40	Water	600 ml
	Ferric organic acid complex salt (shown in Table 2)	0.15 mole
	Thiosulfate	0.6 mole
	Sulfite	0.15 mole
	1,3-Propanediaminetetraacetic acid	2 g
45	adjusted to pH 7.0 by suitably using aqueous ammonia, potassium hydroxide or acetic acid, and made up to 1 liter in total.	

As shown in Table 2, ammonium salts and potassium salts of the above additives (ferric organic acid complex salt, thiosulfate and sulfite) were used suitably for controlling the ratio (mole %) of ammonium ion in the bleach-fixing solution.

Bleach-fixing replenishing solution

In the above bleach-fixing solution, each concentration of the respective additives was increased by 1.25 times and each pH was made 5.8.

Stabilizing solution and replenishing solution	
Orthophenylphenol	0.1 g
Uvitex MST (trade name) (produced by Ciba Geigy AG)	1.0 g
ZnSO ₄ • 7H ₂ O	0.1 g
Ammonium sulfite (40 % solution)	5.0 ml
1-Hydroxyethylidene-1,1-diphosphonic acid (60 % solution)	3.0 g
Ethylenediaminetetraacetic acid	1.5 g
adjusted to pH 7.8 with aqueous ammonia or sulfuric acid, and made up to 1 liter with water.	

By using the color paper and processing solutions prepared, running processing was carried out.

The running processing was carried out by charging an automatic processor with the above color developing tank solution, bleach-fixing tank solution and stabilizing tank solution, and processing the above light-sensitive color photographic material while replenishing the above color developing replenishing solution, bleach-fixing replenishing solution and stabilizing replenishing solution through metering pumps at intervals of 3 minutes.

The running processing was carried out continuously until the amount of the bleach-fixing replenishing solution replenished to the bleach-fixing tank solution became a 3-fold volume of that of the bleach-fixing tank solution. "1R" means that the bleach-fixing replenishing solution is replenished in an amount of a bleach-fixing tank volume.

After the processing, the residual silver quantity at an exposed portion of the color paper was measured by fluorescent X ray. Further, stain at an edge portion of the processed light-sensitive color photographic material after completion of the running test was observed. Also, the state of the bleach-fixing tank solution at the time of completion of the running processing (generation of sulfide) was evaluated visually. These results are shown in Table 2.

In Table 2, symbols in the columns of "Generation of sulfide" have the following meanings.

- ⊙: No sulfide is observed at all.
- O: Floating materials are extremely slightly observed at a liquid surface.
- Δ: Generation of sulfide is slightly observed.
- X: Generation of sulfide is clearly observed.
- XX: Generation of a large amount of sulfide is observed.

Symbols in the columns of "Stain at edge" have the following meanings.

- ⊙: Stain at an edge is not observed at all.
- O: Stain at an edge is extremely slightly observed.
- Δ: Stain at an edge is slightly observed.
- X: Stain at an edge which becomes a problem is observed.
- XX: Remarkable stain at an edge is observed.

Table 2

Experi- ment No.	Ferric organic acid complex salt	Ratio of ammonium ion to whole cation in bleach-fixing solution (mole %)	Residual silver quantity (mg/100 cm ²)	Stain at edge	Generation of sulfide	Remarks
2-1	EDTA·Fe	100	0.9	Δ	X	Comparison
2-2	EDTA·Fe	60	0.9	Δ	X	Comparison
2-3	EDTA·Fe	50	1.0	Δ	X	Comparison
2-4	EDTA·Fe	30	1.0	O	X	Comparison
2-5	EDTA·Fe	10	1.1	O	X	Comparison
2-6	EDTA·Fe	0	1.2	O	X	Comparison
2-7	PDTA·Fe	100	1.8	Δ	XX	Comparison
2-8	PDTA·Fe	60	1.9	Δ	XX	Comparison
2-9	PDTA·Fe	50	1.9	O	XX	Comparison
2-10	PDTA·Fe	30	2.1	O	XX	Comparison
2-11	PDTA·Fe	10	2.0	O	XX	Comparison
2-12	PDTA·Fe	0	2.2	O	XX	Comparison
2-13	DTPA·Fe	100	0	XX	O	Comparison
2-14	DTPA·Fe	60	0	XX	O	Comparison
2-15	DTPA·Fe	50	0.1	XX	O	Comparison
2-16	DTPA·Fe	30	0.1	XX	O	Comparison
2-17	DTPA·Fe	10	0.2	X	O	Comparison
2-18	DTPA·Fe	0	0.2	X	O	Comparison

Table 2 (cont'd)

Experi- ment No.	Ferric organic acid complex salt	Ratio of ammonium ion to whole cation in bleach-fixing solution (mole %)	Residual silver quantity (mg/100 cm ²)	Stain at edge	Generation of sulfide	Remarks
2-19	NTA·Fe	100	1.3	Δ	X	Comparison
2-20	NTA·Fe	60	1.3	Δ	X	Comparison
2-21	NTA·Fe	50	1.4	O	X	Comparison
2-22	NTA·Fe	30	1.5	O	X	Comparison
2-23	NTA·Fe	10	1.7	O	X	Comparison
2-24	NTA·Fe	0	1.8	O	X	Comparison
2-25	(I-1)·Fe	100	0.2	Δ	O	Present invention
2-26	(I-1)·Fe	60	0.2	Δ	O	Present invention
2-27	(I-1)·Fe	50	0.3	Δ to O	O	Present invention
2-28	(I-1)·Fe	30	0.4	O	O	Present invention
2-29	(I-1)·Fe	10	0.4	O	O to ●	Present invention
2-30	(I-1)·Fe	0	0.4	O	●	Present invention

Table 2 (cont'd)

Experiment No.	Ferric organic acid complex salt	Ratio of ammonium ion to whole cation in bleach-fixing solution (mole %)	Residual silver quantity (mg/100 cm ²)	Stain at edge	Generation of sulfide	Remarks
2-31	(I-2)·Fe	100	0.1	Δ	○	Present invention
2-32	(I-2)·Fe	60	0.1	Δ	○	Present invention
2-33	(I-2)·Fe	50	0.2	Δ to ○	○	Present invention
2-34	(I-2)·Fe	30	0.2	Δ to ○	○	Present invention
2-35	(I-2)·Fe	10	0.3	○	○ to ●	Present invention
2-36	(I-2)·Fe	0	0.3	○	●	Present invention
2-37	(I-3)·Fe	100	0.1	Δ	○	Present invention
2-38	(I-3)·Fe	60	0.2	Δ	○	Present invention
2-39	(I-3)·Fe	50	0.2	Δ to ○	○	Present invention
2-40	(I-3)·Fe	30	0.3	Δ to ○	○ to ●	Present invention
2-41	(I-3)·Fe	10	0.4	○	○ to ●	Present invention
2-42	(I-3)·Fe	0	0.4	●	●	Present invention

In Table 2 and the following tables, "EDTA·Fe" represents a ferric complex salt of ethylenediaminetetraacetic acid, "PDTA·Fe" a ferric complex salt of 1,3-propylenediaminetetraacetic acid, "DTPA·Fe" a ferric complex salt of diethylenetriaminepentaacetic acid, "NTA·Fe" a ferric complex salt of nitrilotriacetic acid, "(I-1)·Fe" a ferric complex salt of Exemplary compound (I-1), "(I-2)·Fe" a ferric complex salt of Exemplary compound (I-2) and "(I-3)·Fe" a ferric complex salt of Exemplary compound (I-

3), respectively.

From Table 2 shown above, it can be seen that when the ferric complex salt of the organic acid of the present invention is used, the residual silver quantity is small, the stain at an edge portion is prevented, and the storability of the bleach-fixing solution is good. Further, it can be seen that the above effects are exhibited more favorably when the ratio of ammonium ion to whole cation in the bleach-fixing solution is 50 mole % or less, exhibited particularly favorably when the ratio is 30 mole % or less, and exhibited most favorably when the ratio is 10 mole % or less.

Example 2

In the following Examples, amounts added to a light-sensitive silver halide photographic material are represented by gram per 1 m² of a light-sensitive material unless otherwise indicated. Further, silver halide and colloidal silver are represented by calculating them on silver. A light-sensitive silver iodobromide color photographic material (color film) was prepared as described below.

Light-sensitive silver iodobromide color photographic material

One surface (front surface) of a triacetyl cellulose film support (60 μ m) was subjected to subbing treatment, and on the opposite surface (back surface) beyond the support to the surface subjected to subbing treatment, the respective layers having the following compositions were formed successively from a support side.

Back surface first layer		
Alumina Sol AS-100 (aluminum oxide) (trade name, produced by Nissan Chemical Industries, Ltd.)		0.8 g

Back surface second layer		
Diacetyl cellulose		100 mg
Stearic acid		10 mg
Silica fine grain (average grain size: 0.2 μ m)		50 mg

Subsequently, on the surface of the triacetyl cellulose film support subjected to subbing treatment, the respective layers having the following compositions were formed successively from a support side to prepare a multilayer light-sensitive color photographic material.

First layer: Antihalation layer		
Black colloidal silver		0.15 g
UV absorber (UV-1)		0.20 g
Colored cyan coupler (CC-1)		0.02 g
High boiling point solvent (Oil-1)		0.20 g
High boiling point solvent (Oil-2)		0.20 g
Gelatin		1.6 g

Second layer: Intermediate layer		
Gelatin		1.3 g

Third layer: Low sensitivity red-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.3 μm)	0.4 g
Silver iodobromide emulsion (average grain size: 0.4 μm)	0.3 g
Sensitizing dye (S-1)	3.0×10^{-4} (mole/mole of silver)
Sensitizing dye (S-2)	3.2×10^{-4} (mole/mole of silver)
Sensitizing dye (S-3)	0.3×10^{-4} (mole/mole of silver)
Cyan coupler (C-1)	0.60 g
Cyan coupler (C-2)	0.20 g
Colored cyan coupler (CC-1)	0.07 g
DIR compound (D-1)	0.006 g
DIR compound (D-2)	0.01 g
High boiling point solvent (Oil-1)	0.55 g
Gelatin	1.0 g

Fourth layer: High sensitivity red-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.7 μm)	0.9 g
Sensitizing dye (S-1)	1.7×10^{-4} (mole/mole of silver)
Sensitizing dye (S-2)	1.6×10^{-4} (mole/mole of silver)
Sensitizing dye (S-3)	0.2×10^{-4} (mole/mole of silver)
Cyan coupler (C-2)	0.23 g
Colored cyan coupler (CC-1)	0.03 g
DIR compound (D-2)	0.02 g
High boiling point solvent (Oil-1)	0.30 g
Gelatin	1.0 g

Fifth layer: Intermediate layer

Gelatin	0.8 g
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Sixth layer: Low sensitivity green-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.4 μm)	0.6 g
Silver iodobromide emulsion (average grain size: 0.3 μm)	0.2 g
Sensitizing dye (S-4)	6.7×10^{-4} (mole/mole of silver)
Sensitizing dye (S-5)	1.0×10^{-4} (mole/mole of silver)
Magenta coupler (M-A)	0.20 g
Magenta coupler (M-B)	0.40 g
Colored magenta coupler (CM-1)	0.10 g
DIR compound (D-3)	0.02 g
High boiling point solvent (Oil-2)	0.7 g
Gelatin	1.0 g

Seventh layer: High sensitivity green-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.7 μm)	0.9 g
Sensitizing dye (S-6)	1.1×10^{-4} (mole/mole of silver)
Sensitizing dye (S-7)	2.0×10^{-4} (mole/mole of silver)
Sensitizing dye (S-8)	0.5×10^{-4} (mole/mole of silver)
Magenta coupler (M-A)	0.5 g
Magenta coupler (M-B)	0.13 g
Colored magenta coupler (CM-1)	0.04 g
DIR compound (D-3)	0.004 g
High boiling point solvent (Oil-2)	0.35 g
Gelatin	1.0 g

Eighth layer: Yellow filter layer

Yellow colloidal silver	0.1 g
Additive (HS-1)	0.07 g
Additive (HS-2)	0.07 g
Additive (SC-1)	0.12 g
High boiling point solvent (Oil-2)	0.15 g
Gelatin	0.9 g

Ninth layer: Low sensitivity blue-sensitive emulsion layer

Silver iodobromide emulsion (average grain size: 0.3 μm)	0.25 g
Silver iodobromide emulsion (average grain size: 0.4 μm)	0.25 g
Sensitizing dye (S-9)	5.8×10^{-4} (mole/mole of silver)
Yellow coupler (Y-1)	0.71 g
Yellow coupler (Y-2)	0.30 g
DIR compound (D-1)	0.003 g
DIR compound (D-2)	0.006 g
High boiling point solvent (Oil-2)	0.18 g
Gelatin	1.2 g

Tenth layer: High sensitivity blue-sensitive emulsion layer

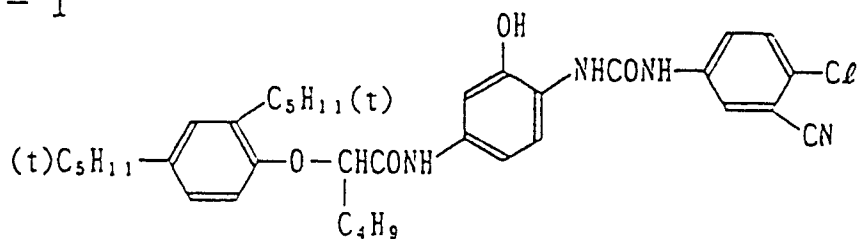
Silver iodobromide emulsion (average grain size: 0.8 μm)	0.5 g
Sensitizing dye (S-10)	3×10^{-4} (mole/mole of silver)
Sensitizing dye (S-11)	1.2×10^{-4} (mole/mole of silver)
Yellow coupler (Y-1)	0.18 g
Yellow coupler (Y-2)	0.20 g
High boiling point solvent (Oil-2)	0.05 g
Gelatin	0.9 g

Eleventh layer: First protective layer	
Silver iodobromide (average grain size: 0.08 μm)	0.3 g
UV absorber (UV-1)	0.07 g
UV absorber (UV-2)	0.10 g
Additive (HS-1)	0.2 g
Additive (HS-2)	0.1 g
High boiling point solvent (Oil-1)	0.07 g
High boiling point solvent (Oil-3)	0.07 g
Gelatin	0.85 g

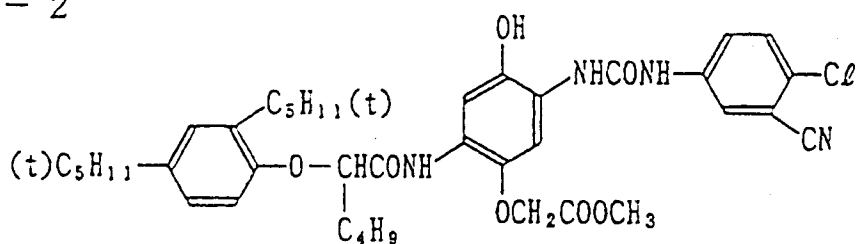
Twelfth layer: Second protective layer	
Compound A	0.04 g
Compound B	0.004 g
Polymethyl methacrylate (average grain size: 3 μm)	0.02 g
Copolymer of methyl methacrylate:ethyl methacrylate:methacrylic acid = 3:3:4 (weight ratio) (average grain size: 3 μm)	0.13 g

In the above light-sensitive silver iodobromide color photographic material, Compounds Su-1 and Su-2, a viscosity controller, Hardeners H-1 and H-2, Stabilizer ST-1, Anti-foggants AF-1 and AF-2 (having weight average molecular weights of 10000 and 1100000), Dyes AI-1 and AI-2, and Compound DI-1 (9.4 mg/m²) were further contained.

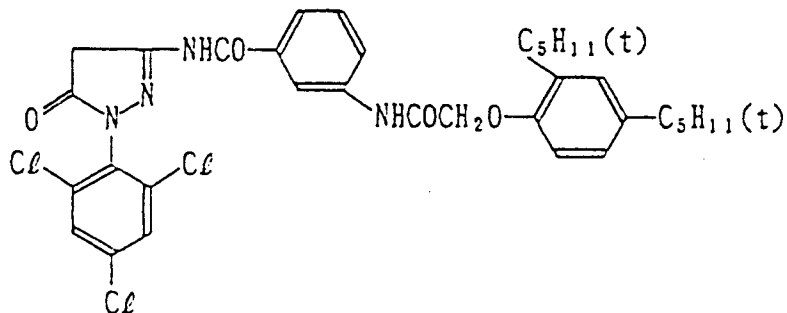
C - 1



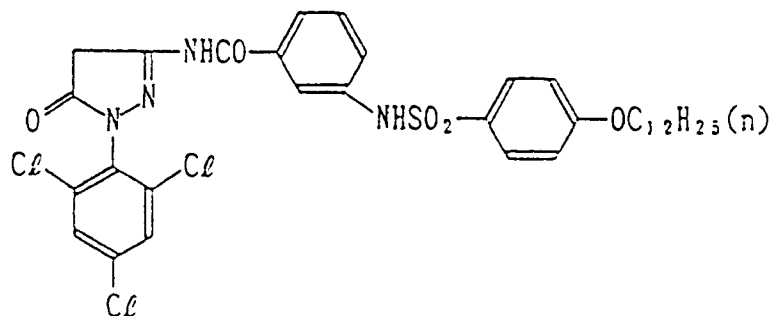
C - 2



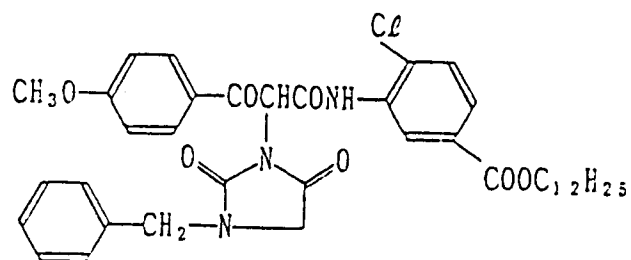
M - A



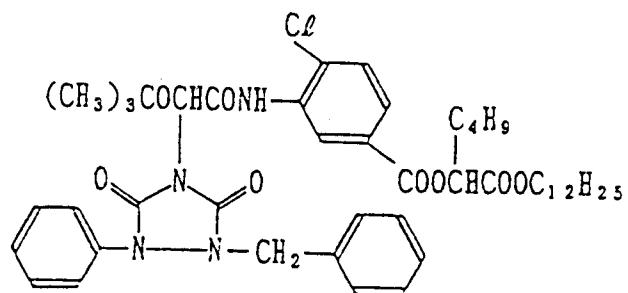
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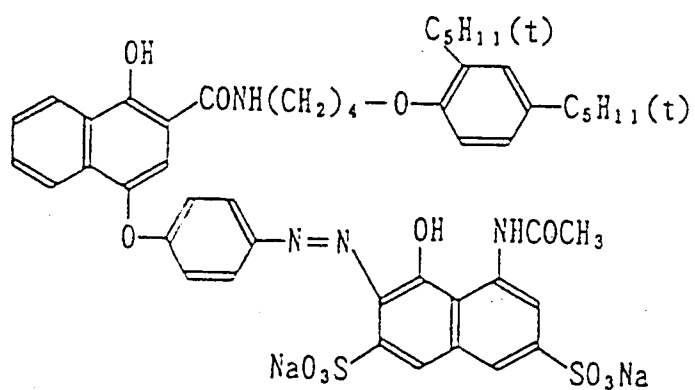
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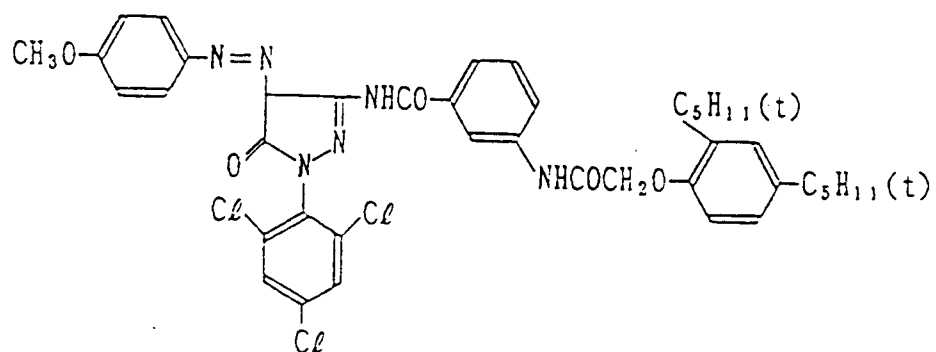
Y - 2



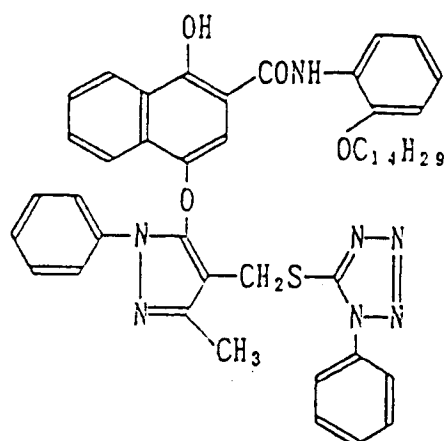
CC - 1



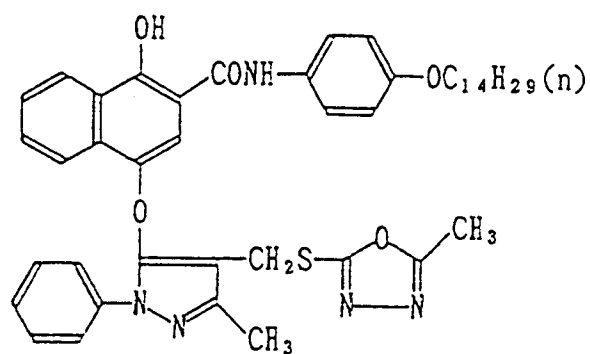
CM - 1



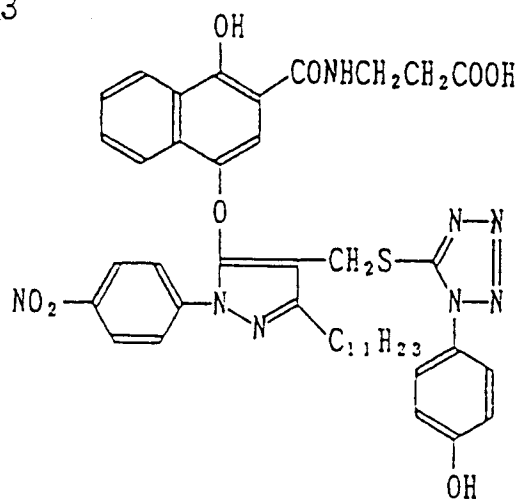
D - 1



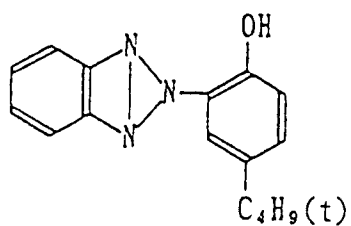
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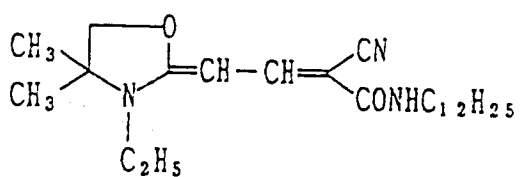
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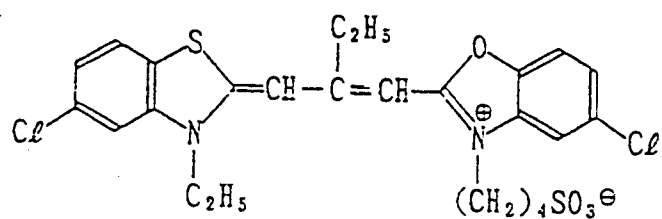
U V - 1



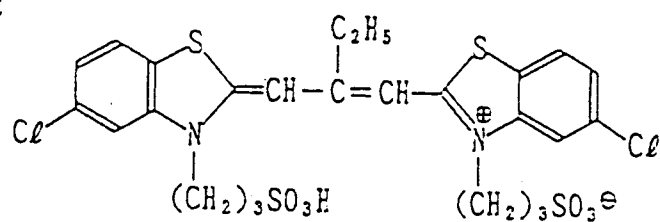
U V - 2



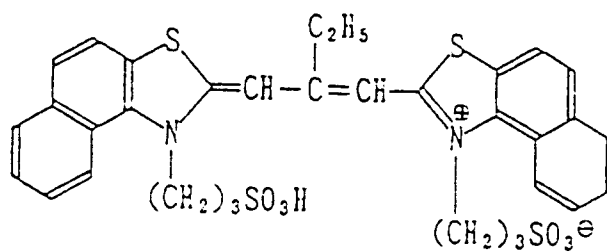
S - 1



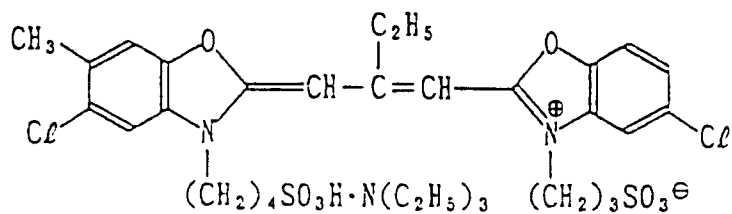
S - 2



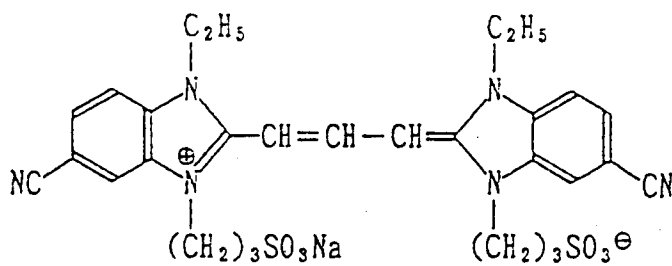
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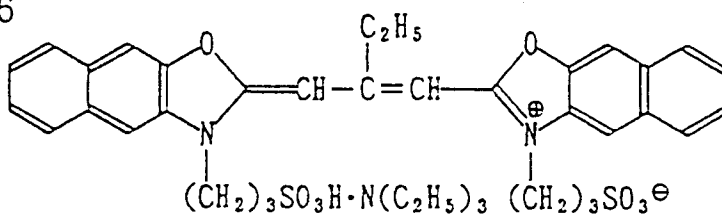
S - 4



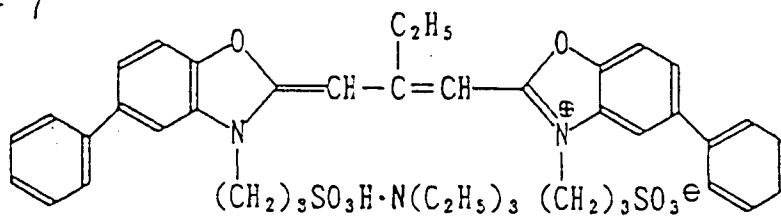
S - 5



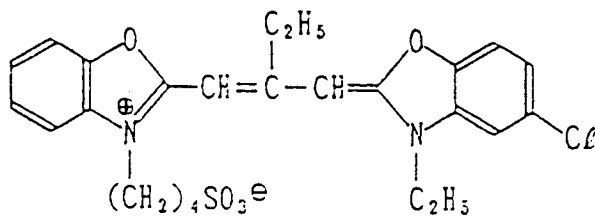
S - 6



S - 7



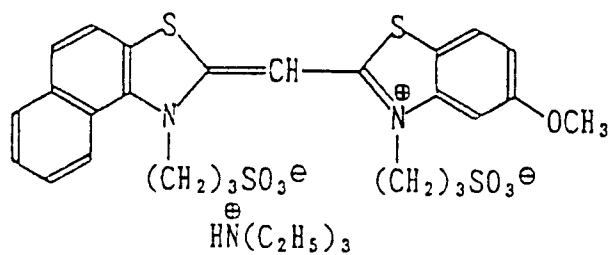
S - 8



S - 9

5

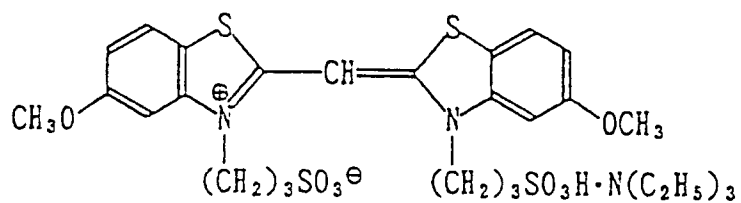
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S - 10

15

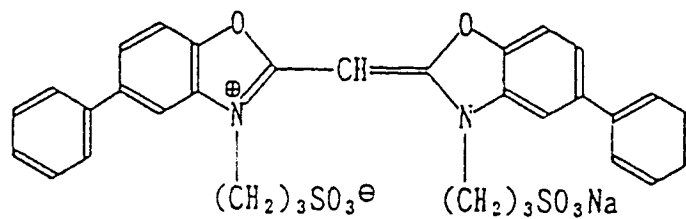
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S - 11

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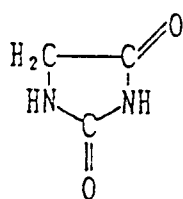
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35

H S - 1

40

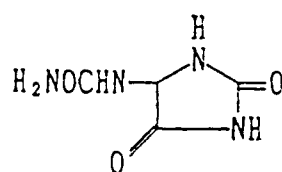


45

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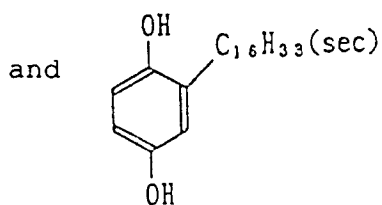
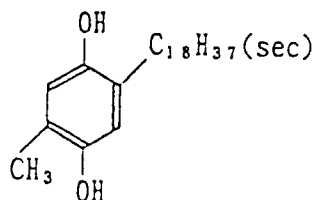
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H S - 2

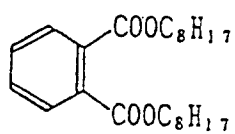


SC-1

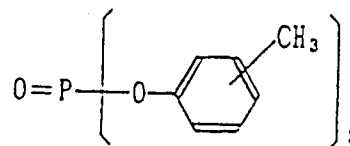
Mixture (2:3) of



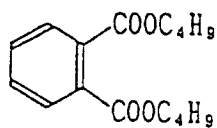
Oil-1



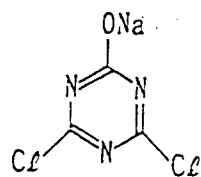
Oil-2



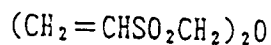
Oil-3



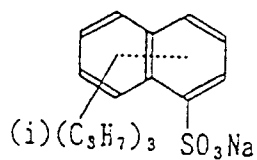
H-1



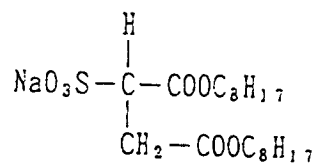
H-2



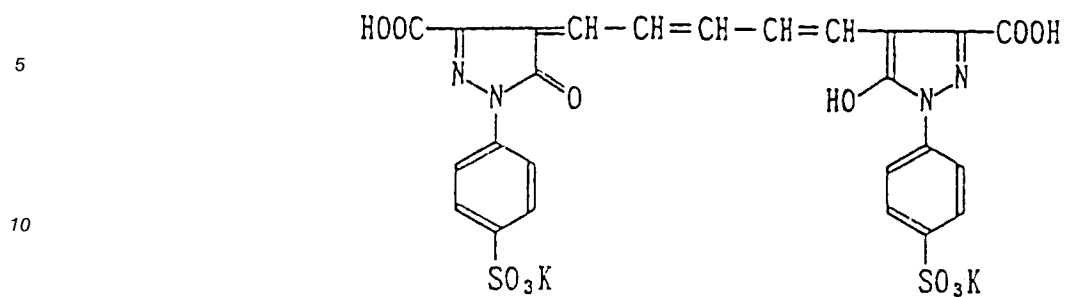
SU-1



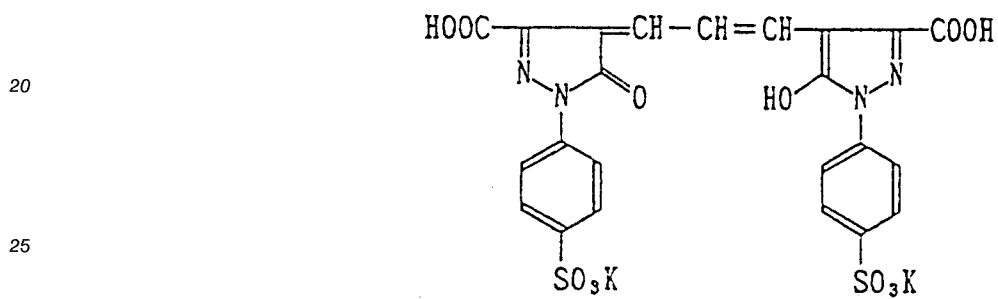
SU-2



A I - 1



A I - 2



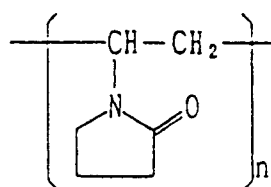
S T - 1



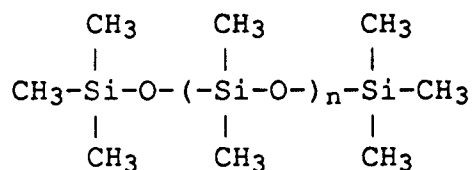
A F - 1



A F - 2

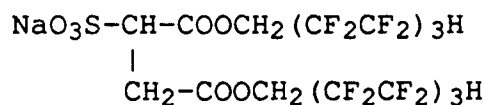


Compound A

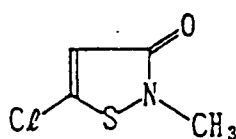


Weight average molecular weight = 30000

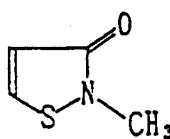
Compound B



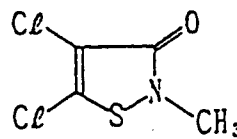
DI-1 (mixture of three components shown below)



(Component A)



(Component B)



(Component C)

Component A:Component B:Component C = 50:23:27 (molar ratio)

(Preparation of emulsion)

The silver iodobromide emulsion used in the tenth layer was prepared as described below.

The silver iodobromide emulsion was prepared by the double jet method by using a monodispersed silver iodobromide grain having an average grain size of 0.33 μm (silver iodide content: 2 mole %) as a seed crystal.

To Solution (G-1) maintained at a temperature of 70 °C, pAg 7.8 and pH 7.0 was added a seed emulsion in an amount corresponding to 0.34 mole while stirring well.

(Formation of phase having inner portion high in iodide content - core phase)

Thereafter, while maintaining a flow ratio of 1:1, (H-1) and (S-1) were added over 86 minutes at an accelerated flow rate (the flow rate at the time of completion of addition was 3.6 times of the initial flow rate).

(Formation of phase having outer portion low in iodide content - shell phase)

Subsequently, while maintaining pAg 10.1 and pH 6.0, (H-2) and (S-2) at a flow ratio of 1:1 were added over 65 minutes at an accelerated flow rate (the flow rate at the time of completion of addition was 5.2 times of the initial flow rate).

During formation of grains, the pAg and pH were controlled by using a potassium bromide aqueous solution and a 56 % acetic acid aqueous solution. After formation of grains, the grains were subjected to washing processing according to a conventional flocculation method. Then, the grains were added to gelatin and redispersed, and the pH and pAg were adjusted to 5.8 and 8.06, respectively, at 40 ° C.

The emulsion obtained was a monodispersed emulsion containing an octahedral silver iodobromide grain having an average grain size of 0.80 μm , a variation coefficient of a grain size distribution of 12.4 % and a silver iodide content of 9.0 mole %.

(G-1)	
Ossein gelatin	100.0 g
10 % by weight methanol solution of Compound-1	25.0 ml
28 % Aqueous ammonia	440.0 ml
56 % Acetic acid aqueous solution	660.0 ml
made up to 5000.0 ml with water.	

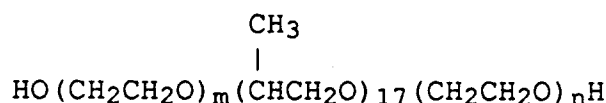
(H-1)	
Ossein gelatin	82.4 g
Potassium bromide	151.6 g
Potassium iodide	90.6 g
made up to 1030.5 ml with water.	

(S-1)	
Silver nitrate	309.2 g
28 % Aqueous ammonia	Equivalent amount
made up to 1030.5 ml with water.	

(H-2)	
Ossein gelatin	302.1 g
Potassium bromide	770.0 g
Potassium iodide	33.2 g
made up to 3776.8 ml with water.	

(S-2)	
Silver nitrate	1133.0 g
28 % Aqueous ammonia	Equivalent amount
made up to 3776.8 ml with water.	

Compound-1



(Weight average molecular weight $\approx$ 1300) wherein m and n each represent a natural number up to 30, which may be the same or different.

In the same manner as described above, the above respective emulsions having different average grain sizes and silver iodide contents were prepared by changing an average grain size of a seed crystal, temperature, pAg, pH, flow rate, addition time and halide composition.

Either of them was a core/shell type monodispersed emulsion having a variation coefficient of a grain size distribution of 20 % or less. The respective emulsions were applied to optimum chemical ripening in the presence of sodium thiosulfate, chloroauric acid and ammonium thiocyanate, and a sensitizing dye, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 1-phenyl-5-mercaptotetrazole were added.

However, the above light-sensitive silver iodobromide color photographic material was prepared so as to have an average silver iodide content of 8 mole %.

The light-sensitive material thus prepared was subjected to wedge exposure according to a conventional method, and then running processing according to the following processing steps. The running processing was carried out continuously until the amount of the bleach-fixing replenishing solution became a 2-fold volume of a bleach-fixing tank volume (2R).

Processing step	Processing time	Processing temperature	Amount replenished (per 135 size 24 EX1)
(1) Color developing	3 min 15 sec	38 °C	20 ml
(2) Bleach-fixing	3 min 15 sec	38 °C	30 ml
(3) Stabilizing (3 tank cascade)	1 min	38 °C	40 ml
(4) Drying	1 min	40 to 80 °C	

Color developing solution	
Potassium carbonate	30.0 g
Sodium hydrogen carbonate	2.5 g
Potassium sulfite	3.0 g
Sodium bromide	1.3 g
Potassium iodide	1.2 mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)-aniline sulfate	4.5 g
Diethylenetriaminepentaacetic acid	3.0 g
Potassium hydroxide	1.2 g
made up to 1 liter with addition of water, and adjusted to pH 10.00 with potassium hydroxide or 20 % sulfuric acid.	

Color developing replenishing solution	
Potassium carbonate	35 g
Sodium hydrogen carbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.5 g
Hydroxylamine sulfate	3.5 g
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)-aniline sulfate	6.0 g
Potassium hydroxide	2 g
Diethylenetriaminepentaacetic acid	3.0 g
made up to 1 liter with addition of water, and adjusted to pH 10.12 with potassium hydroxide or 20 % sulfuric acid.	

Bleach-fixing tank solution	
Water	600 ml
Ferric organic acid complex salt (shown in Table 3)	0.4 mole
Thiosulfate	2.0 mole
Sulfite	0.15 mole
1,3-Propanediaminetetraacetic acid	2 g
adjusted to pH 7.0 with aqueous ammonia or acetic acid, and made up to 1 liter in total.	

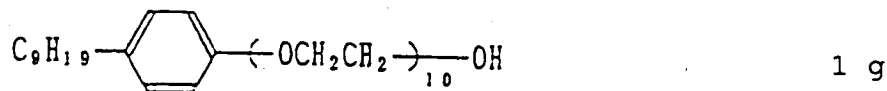
As shown in Table 3, ammonium salts and potassium salts of the above additives (ferric organic acid complex salt, thiosulfate and sulfite) were used suitably for controlling the ratio (mole %) of ammonium ion in the bleach-fixing solution.

Bleach-fixing replenishing solution

In the above bleach-fixing tank solution, each concentration of the respective additives was increased by 1.07 times, and each pH was made 6.0.

Stabilizing solution (tank solution and replenishing solution)

o-Phenylphenol	0.5 g
Hexamethylenetetramine	5.0 g
Diethylene glycol	10 g



adjusted to pH 8.0 with KOH, and made up to 1 liter with addition of water.

In the same manner as in Example 1, running processing was carried out, and the residual silver quantity and sulfurization of the bleach-fixing solution after processing were evaluated.

The results are shown in Table 3.

Table 3

Experi- ment No.	Ferric organic acid complex salt	Ratio of ammonium ion to whole cation in bleach-fixing solution (mole %)	Residual silver quantity (mg/100 cm ²)	Generation of sulfide	Remarks
2-1	EDTA·Fe	100	4.8	X	Comparison
2-2	EDTA·Fe	60	5.0	X	Comparison
2-3	EDTA·Fe	50	5.2	X	Comparison
2-4	EDTA·Fe	30	5.2	X	Comparison
2-5	EDTA·Fe	10	5.3	X	Comparison
2-6	EDTA·Fe	0	5.4	X	Comparison
2-7	PDTA·Fe	100	7.8	XX	Comparison
2-8	PDTA·Fe	60	8.2	XX	Comparison
2-9	PDTA·Fe	50	8.6	XX	Comparison
2-10	PDTA·Fe	30	9.0	XX	Comparison
2-11	PDTA·Fe	10	9.3	XX	Comparison
2-12	PDTA·Fe	0	9.5	XX	Comparison
2-13	NTA·Fe	100	5.2	X	Comparison
2-14	NTA·Fe	60	5.8	X	Comparison
2-15	NTA·Fe	50	6.0	X	Comparison
2-16	NTA·Fe	30	6.1	X	Comparison
2-17	NTA·Fe	10	6.2	X	Comparison
2-18	NTA·Fe	0	6.3	X	Comparison

Table 3 (cont'd)

Experi- ment No.	Ferric organic acid complex salt	Ratio of ammonium ion to whole cation in bleach-fixing solution (mole %)	Residual silver quantity (mg/100 cm ²)	Generation of sulfide	Remarks
2-19	(I-1)·Fe	100	0.3	Δ to 0	Present invention
2-20	(I-1)·Fe	60	0.6	Δ to 0	Present invention
2-21	(I-1)·Fe	50	0.7	0	Present invention
2-22	(I-1)·Fe	30	0.7	0	Present invention
2-23	(I-1)·Fe	10	0.8	●	Present invention
2-24	(I-1)·Fe	0	0.8	●	Present invention
2-25	(I-4)·Fe	100	0.2	Δ to 0	Present invention
2-26	(I-4)·Fe	60	0.2	Δ to 0	Present invention
2-27	(I-4)·Fe	50	0.4	0	Present invention
2-28	(I-4)·Fe	30	0.4	0	Present invention
2-29	(I-4)·Fe	10	0.6	0 to ●	Present invention
2-30	(I-4)·Fe	0	0.7	●	Present invention
2-31	(I-5)·Fe	100	0.2	Δ	Present invention
2-32	(I-5)·Fe	60	0.3	Δ to 0	Present invention
2-33	(I-5)·Fe	50	0.4	0	Present invention
2-34	(I-5)·Fe	30	0.4	0	Present invention
2-35	(I-5)·Fe	10	0.6	0	Present invention
2-36	(I-5)·Fe	0	0.8	0	Present invention

In Table 3, "(I-4)·Fe" represents a ferric complex salt of Exemplary compound (I-4), and "(I-5)·Fe" a ferric complex salt of Exemplary compound (I-5).

From Table 3 shown above, it can be seen that when the ferric complex salt of the organic acid of the present invention is used, the silver quantity is small, and the storability of the bleach-fixing solution is good. Further, it can be seen that the above effects are exhibited more favorably when the ratio of ammonium ion to whole cation in the bleach-fixing solution is 50 mole % or less, exhibited particularly favorably when the

ratio is 30 mole % or less, and exhibited most favorably when the ratio is 10 mole % or less.

Example 3

- 5 Experiments were carried out in the same manner as in Example 2 except for changing the processing steps as shown below and changing the bleaching solution and the fixing solution to the processing solutions having the compositions shown below. (A processing round number per one day was 0.05 R (with respect to the bleaching solution).)

10	Processing step	Processing time	Processing temperature	Amount replenished (per 135 size 24 EX1)
	(1) Color developing (one tank)	3 min 15 sec	38 ° C	20 ml
	(2) Bleaching (one tank)	45 sec	38 ° C	5 ml
15	(3) Fixing (one tank)	1 min 30 sec	38 ° C	33 ml
	(4) Stabilizing (3 tank cascade)	1 min	38 ° C	40 ml
	(4) Drying	1 min	40 to 80 ° C	

20	Bleaching tank solution	
	Water	600 ml
	Ferric organic acid complex salt (shown in Table 4)	0.35 mole
25	Ethylenediaminetetraacetic acid	10 g
	Bromide	1.3 mole
	Glacial acetic acid	50 ml
	adjusted to pH 4.5 with aqueous ammonia and acetic acid, and made up to 1 liter with addition of water.	

- 30 As shown in Table 4, ammonium salts and potassium salts of the above additives (ferric organic acid complex salt and bromide) were used suitably for controlling the ratio (mole %) of ammonium ion in the bleaching solution.

35 Bleaching replenishing solution

In the above bleaching tank solution, each concentration of the respective additives was increased by 1.2 times, and each pH was made 3.5.

40	Fixing solution (tank solution and replenishing solution)	
	Ammonium thiosulfate (70 % solution)	350 ml
	Anhydrous sodium bisulfite	12 g
	Sodium metabisulfite	2.5 g
45	Disodium ethylenediaminetetraacetate	0.5 g
	made up to 1 liter with addition of water, and adjusted to pH 6.5 with acetic acid and aqueous ammonia.	

- 50 After continuous processing, the magenta transmission density (green light density) at an unexposed portion of the film sample was measured, and at the same time, the residual silver quantity at an exposed portion was measured by a fluorescent X ray method.

The results obtained above are shown in Table 4.

Table 4

Experiment No.	Ferric organic acid complex salt	Ratio of ammonium ion to whole cation in bleach-fixing solution (mole %)	Residual silver quantity (mg/100 cm ²)	Magenta transmission density at unexposed portion	Remarks
3-1	EDTA·Fe	100	7.5	0.57	Comparison
3-2	EDTA·Fe	60	7.5	0.57	Comparison
3-3	EDTA·Fe	50	7.7	0.56	Comparison
3-4	EDTA·Fe	30	7.7	0.56	Comparison
3-5	EDTA·Fe	10	7.9	0.56	Comparison
3-6	EDTA·Fe	0	7.9	0.56	Comparison
3-7	PDTA·Fe	100	0	0.63	Comparison
3-8	PDTA·Fe	60	0	0.63	Comparison
3-9	PDTA·Fe	50	0.1	0.61	Comparison
3-10	PDTA·Fe	30	0.1	0.61	Comparison
3-11	PDTA·Fe	10	0.3	0.60	Comparison
3-12	PDTA·Fe	0	0.3	0.60	Comparison
3-13	DTPA·Fe	100	6.8	0.58	Comparison
3-14	DTPA·Fe	60	6.8	0.58	Comparison
3-15	DTPA·Fe	50	6.9	0.57	Comparison
3-16	DTPA·Fe	30	6.9	0.57	Comparison
3-17	DTPA·Fe	10	7.0	0.56	Comparison
3-18	DTPA·Fe	0	7.0	0.56	Comparison

Table 4 (cont'd)

Experiment No.	Ferric organic acid complex salt	Ratio of ammonium ion to whole cation in bleach-fixing solution (mole %)	Residual silver quantity (mg/100 cm ²)	Magenta transmission density at unexposed portion	Remarks
3-19	NTA·Fe	100	8.5	0.58	Comparison
3-20	NTA·Fe	60	8.5	0.58	Comparison
3-21	NTA·Fe	50	8.8	0.57	Comparison
3-22	NTA·Fe	30	8.8	0.57	Comparison
3-23	NTA·Fe	10	9.1	0.57	Comparison
3-24	NTA·Fe	0	9.2	0.57	Comparison
3-25	(I-1)·Fe	100	0.1	0.58	Present invention
3-26	(I-1)·Fe	60	0.1	0.58	Present invention
3-27	(I-1)·Fe	50	0.2	0.57	Present invention
3-28	(I-1)·Fe	30	0.3	0.57	Present invention
3-29	(I-1)·Fe	10	0.3	0.56	Present invention
3-30	(I-1)·Fe	0	0.4	0.56	Present invention
3-31	(I-2)·Fe	100	0.1	0.58	Present invention
3-32	(I-2)·Fe	60	0.1	0.58	Present invention
3-33	(I-2)·Fe	50	0.2	0.57	Present invention
3-34	(I-2)·Fe	30	0.3	0.57	Present invention
3-35	(I-2)·Fe	10	0.3	0.56	Present invention
3-36	(I-2)·Fe	0	0.4	0.56	Present invention

Table 4 (cont'd)

Experi- ment No.	Ferric organic acid complex salt	Ratio of ammonium ion to whole cation in bleach-fixing solution (mole %)	Residual silver quantity (mg/100 cm ²)	Magenta transmis- sion density at unexposed portion	Remarks
3-37	(I-5)·Fe	100	0.2	0.58	Present invention
3-38	(I-5)·Fe	60	0.2	0.58	Present invention
3-39	(I-5)·Fe	50	0.3	0.57	Present invention
3-40	(I-5)·Fe	30	0.3	0.57	Present invention
3-41	(I-5)·Fe	10	0.4	0.56	Present invention
3-42	(I-5)·Fe	0	0.6	0.56	Present invention

From Table 4 shown above, it can be seen that when the ferric complex salt of the organic acid of the present invention is used, the residual silver quantity is small, and increase of the magenta transmission density at an unexposed portion is small. Further, it can be seen that the above effects are exhibited more favorably when the ratio of ammonium ion to whole cation in the bleach-fixing solution is 50 mole % or less, exhibited particularly favorably when the ratio is 30 mole % or less, and exhibited most favorably when the

ratio is 10 mole % or less.

Example 4

For the respective ferric complex salts of a chelating agent which has been generally used for photographs, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), and Exemplary compounds (I-1), (I-2), (I-3), (I-4), (I-5), (I-6) and (I-9), biodegradabilities were determined according to the 301C modified MITI Test (I) of OECD Chemical Product Test Guideline (adopted on May 12, 1981).

As a result, it was found that the biodegradability of the ferric complex salt of the chelating agent of the present invention was extremely good while the ferric complex salts of EDTA, DTPA and HEDTA were not hardly degraded, and therefore the chelating agent of the present invention is extremely preferred from the standpoint of protection of environments of the earth.

Example 5

Experiments were carried out in the same manner as in Example 3 except for adding nitrate (sodium nitrate) to the bleaching solutions used in Experiments No. 3 to No. 29 in Example 3 as shown in Table 5. The results are shown in Table 5.

Table 5

Experiment No.	Amount of sodium nitrate added (g/l)	Residual silver quantity (mg/100 cm ²)	Magenta transmission density at unexposed portion
5-1	0	0.3	0.56
5-2	5	0.2	0.56
5-3	10	0.2	0.55
5-4	20	0.1	0.55
5-5	40	0	0.55
5-6	100	0.2	0.55

From Table 5 shown above, it can be seen that the effect of the present invention can be exhibited more favorably by using the processing solution of the present invention and nitrate in combination.

Example 6

Experiments were carried out in the same manner as in Example 3 except for changing acetic acid in the bleaching solutions used in Experiments No. 3 to No. 35 in Example 3 to the same molar amount of organic acid or inorganic acid shown in Table 6 shown below.

The results are shown in Table 6.

Table 6

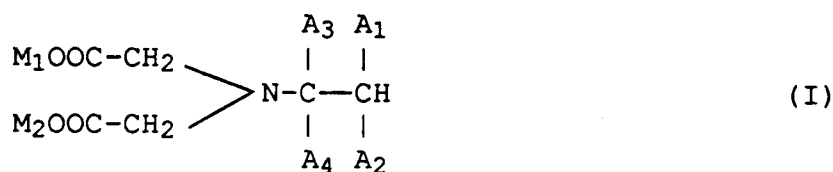
Experiment No.	Organic or inorganic acid	Residual silver quantity (mg/100 cm ²)	Transmission density at unexposed portion
6-1	Acetic acid	0.3	0.56
6-2	Sulfuric acid	0.6	0.58
6-3	Exemplary compound (II-1)	0.2	0.54
6-4	Exemplary compound (II-2)	0.1	0.54
6-5	Exemplary compound (II-4)	0.1	0.54
6-6	Exemplary compound (II-5)	0.1	0.55
6-7	Exemplary compound (II-16)	0	0.54
6-8	Exemplary compound (II-7)	0.1	0.55

From Table 6 shown above, it can be seen that the effect of the present invention can be exhibited more favorably when the compound represented by the above formula (II) was used in combination in the processing solution of the present invention.

According to the present invention, there can be provided a processing solution having bleachability for a light-sensitive silver halide color photographic material, which does not cause bleaching fog, enables rapid processing, has excellent biodegradability and environmental suitability, enables stable processing without causing sulfurization, and prevents yellow stain at an edge portion of a light-sensitive material.

Claims

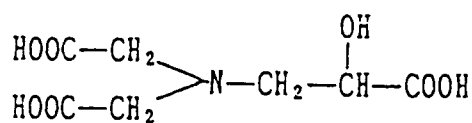
1. A processing solution having bleachability for a light-sensitive silver halide color photographic material, which comprises at least a ferric complex salt of a compound represented by the following formula (I):



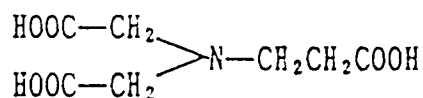
(wherein A_1 , A_2 , A_3 and A_4 may be the same or different, and each represent hydrogen atom, hydroxyl group, $-\text{COOM}$, $-\text{PO}_3\text{M}_2$, $-\text{CH}_2\text{OH}$ or a lower alkyl group; at least one of A_1 , A_2 , A_3 and A_4 is $-\text{COOM}$ or $-\text{PO}_3\text{M}_2$; M , M_1 and M_2 each represent hydrogen atom, ammonium group, sodium atom, potassium atom, lithium atom or an organic ammonium group).

2. The solution of Claim 1 wherein A_1 , A_2 , A_3 and A_4 each represent hydrogen atom, hydroxyl group, $-\text{COOM}$, $-\text{PO}_3\text{M}_2$, $-\text{CH}_2\text{OH}$, methyl group, ethyl group, isopropyl group or n-propyl group and M , M_1 and M_2 each represent hydrogen atom, ammonium group, sodium atom, potassium atom, lithium atom, trimethylammonium group or triethanolammonium group.
3. The solution of Claim 1 wherein the compound represented by the formula (I) is a compound selected from the group consisting of:

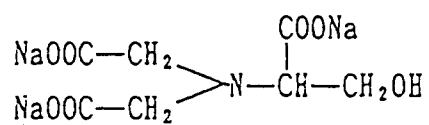
(I-1)



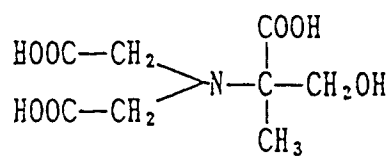
(I-2)



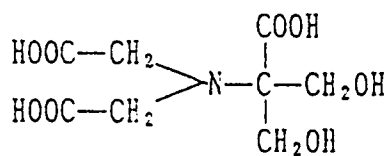
(I-3)



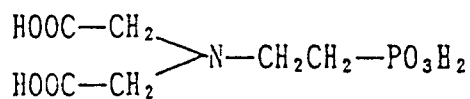
(I-4)



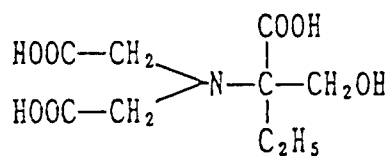
(I-5)



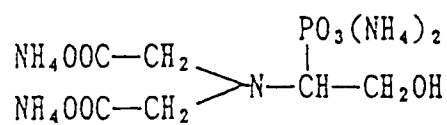
(I-6)



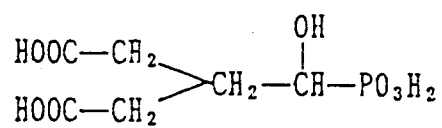
(I-7)



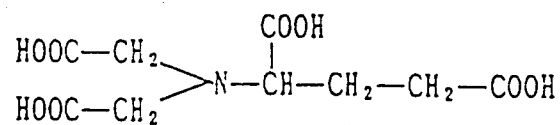
(I-8)



(I-9)

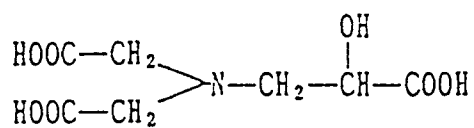


(I-10)

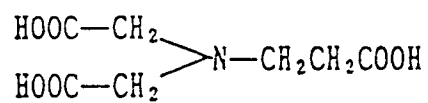


4. The solution of Claim 1 wherein the compound represented by the formula (I) is at least one selected from the group consisting of:

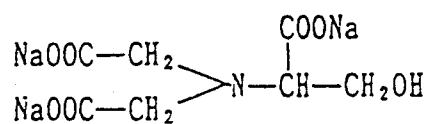
(I-1)



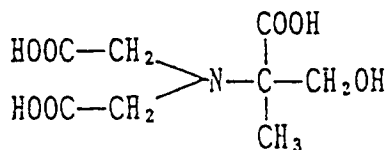
(I-2)



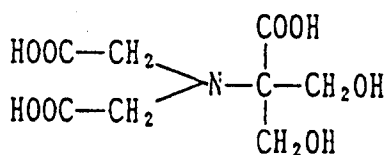
(I-3)



(I-4)



(I-5)



5. The solution of Claim 1 wherein the processing solution is a bleaching solution, a bleach-fixing solution or a bleach-fixing solution for one bath development.
6. The solution of Claim 1 wherein the ferric complex salt is contained in an amount of 0.1 to 2.0 mole per liter of the processing solution.
7. The solution of Claim 1 wherein the ratio of ammonium ion to whole cation in the processing solution is 50 mole % or less.
8. The solution of Claim 1 wherein the processing solution contains nitric acid or a nitrate.
9. The solution of Claim 1 wherein the processing solution contains a compound represented by the following formula (II):



(wherein n represents an integer of 2 to 5; A represents a single bond or an n-valent organic group; M¹ represents hydrogen atom, an alkali metal atom or ammonium group; n M¹'s may be the same or different).

10. The solution of Claim 1 wherein the processing solution contains $\text{HOOCH}=\text{CHCOOH}$.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 2723

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 430 000 (AGFA-GEVAERT AG) * page 14, line 1 - line 20; claims * ---	1-6,8,9	G03C7/42 G03C5/44
X	EP-A-0 270 217 (KONISHIROKU PHOTO INDUSTRY CO.) * page 6, line 17 - line 24 * ---	1-6	
A	* page 19, line 11 - line 27 * ---	1	
X	EP-A-0 199 604 (KONISHIROKU PHOTO INDUSTRY CO.) * col. 5, compounds (2), (9); col. 6, compounds (15),(17); col. 276, sample 8; claims * ---	1-6	
A	DE-A-3 919 551 (AGFA-GEVAERT AG) * abstract * ---	1,8	
D,A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 317 (P-1073)(4260) 9 July 1990 & JP-A-21 03 040 (KONICA CORPORATION) 16 April 1990 * abstract * ---	8	
A	EP-A-0 329 088 (KONICA CORPORATION) * page 17, line 32 * * page 49, Table 1 * ---	1-6,9,10	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C
P,X	EP-A-0 468 325 (AGFA-GEVAERT AG) * page 20, line 15 - line 34 * ---	1-10	
P,A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 35 (P-1304)28 January 1992 & JP-A-32 43 948 (KONICA CORPORATION) 30 October 1991 * abstract * -----	7	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 24 NOVEMBER 1992	Examiner STOCK H.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			