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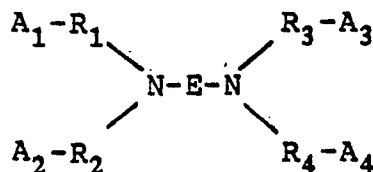
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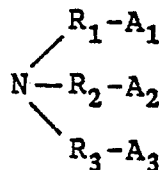
(54) Composition containing ferric complex salt.

(57) An aqueous composition comprising at least 180g per liter of a ferric complex salt of the compound represented by formula (I) or (II) shown below, and having the pH of not more than 7.0;

Formula (I)



Formula (II)



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wherein E represents a substituted or unsubstituted alkylene group, cycloalkylene group or phenylene group, a -R₅OR₅OR₅-group, or a -R₅ZR₅- group; Z represents a $\begin{array}{c} \diagup \\ N-R_5-A_5 \end{array}$ group or a $\begin{array}{c} \diagup \\ N- \end{array}$

R_5 group; R_1 , R_2 , R_3 , R_4 and R_5 independently represent a substituted or unsubstituted alkylene group; A_1 , A_2 , A_3 , A_4 and A_5 independently represent a hydrogen atom, -OH, a -COOM group, or a - PO_3M_2 group; and M represents a hydrogen atom, an alkali metal atom, an ammonium group or a group containing a quaternary ammonium is disclosed.

COMPOSITION CONTAINING FERRIC COMPLEX SALT

FIELD OF THE INVENTION

5 The present invention relates to a composition containing a ferric complex salt, and more particularly to a composition containing a ferric complex salt, suited for use as a composition for photographic processing agents or a part composition for processing agent kits, and having superior long-term storage stability.

10 BACKGROUND OF THE INVENTION

To obtain color images, it is necessary to carry out the so-called desalting that removes metal silver formed together with dye images obtained by color development processing, from light-sensitive silver
15 halide color photographic materials. In general, this desalting is carried out by applying processing steps of making processing with a bleaching solution containing halogen ions and an oxidizing agent to once convert the metal silver to a silver halide, and thereafter making processing in a fixing solution containing a silver halide solvent to remove the silver halide formed by the bleaching, together with the silver halide remaining undeveloped. On the other hand, also known is a processing method of carrying out the processing with the
20 so-called bleach-fixing solution, in which the bleaching and fixing are effected in one solution.

Hitherto used as bleaching agents used in the bleaching of light-sensitive silver halide color photographic materials after color development are compounds such as red prussiate, ferric chloride and organic acid ferric complex salts.

The red prussiate and ferric chloride are good bleaching agents in view of their strong bleaching power,
25 high bleaching rate (rate of oxidation) and capability of sufficiently recoloring even the leuco compound which is an intermediate of a dye. However, the red prussiate is a cyan compound by itself and an aqueous solution thereof may sometimes produce free cyan ions by photolysis, so that a treatment for making waste liquor completely harmless is required when the waste liquor thereof is discharged.

Also, a bleaching solution using the ferric chloride, which has so a very low pH and an extremely strong
30 oxidizing is disadvantageous in that it has a strong corrosive action against metals constituting a processing machine in which the solution is put, and also forms iron hydroxide in the washing step after bleaching to generate the so-called stains in light-sensitive materials.

Known as a bleaching agent that may cause less environmental problems and make easy the reproduction processing as compared with the above red prussiate and ferric chloride are organic ferric
35 complex salts, among which particularly ethylenediaminetetraacetic acid ferric complex salts superior in both the bleaching performance and stability have been put into practical use.

Recent years, with spread of color photographs, there are increasing demands for making rapid the development processing, and also there are striking rises of mini photofinishing laboratories for shop processing or the like because of the decentralization of development processing, so that it has been
40 sought after to simplify the processing management besides making rapid the processing. As a concrete measure therefor, it may be mentioned to simplify the operations for dissolving processing agents. Usually used are the so-called processing agent kits in which the processing agents to be used are beforehand mixed in a given quantity ratio and which can be used by merely adding water to make a homogeneous solution when used, and there are available solid powder type and the so-called liquid type having been
45 brought into the state of a concentrated solution. Preferred, however, is the liquid type in order to simplify the dissolving operations. Already known as the liquid type kits are developing solutions, bleaching solutions, fixing solutions, bleach-fixing solutions, stabilizing solutions, etc., a problem of which, however, is to make concentration without causing decomposition or deposition during storage. Improvements for making concentration are progressed also in the instances of the bleaching solution and bleach-fixing
50 solutions, and Japanese Unexamined Patent Publication No. 52748/1981 employs a method in which a concentrated kit of a bleach-fixing solution is divided into the part containing the bleaching agent aminopolycarboxylic acid ferric complex salt and the part containing the fixing agent thiosulfate in order to stably store the kit.

Japanese Unexamined Patent Publications No. 62129/1974 and No. 95236/1973 also employ a method in which in order to enhance the solubility in respect of an alkali metal salt, having a low solubility, of the

bleaching agent aminopolycarboxylic acid ferric complex salt in the bleach-fixing solution, the pH of the part containing the aminopolycarboxylic acid ferric complex salt is previously raised and the other part is made acidic, whereby a solution for use, having an appropriate pH, is prepared after mixing and dilution. Like this, in respect of the ethylenediaminetetraacetic acid ferric complex salts, among aminopolycarboxylic acid ferric complex salts, usually used in the bleaching solutions and bleach-fixing solutions, the solubility is so low that there have been employed the method in which the pH is made higher and then the kit is concentrated. However, the researches made by the present inventors revealed that such a liquid kit has the disadvantage that under the high pH a decomposition reaction takes place inside the aminopolycarboxylic acid during storage for a long period of time to generate aminopolycarboxylic acid ferrous complex salts.

Moreover, for the purpose of further enhancing the bleaching performance, it has been recently proposed to use as the bleaching agent, aminopolycarboxylic acid ferric complex salts having a larger molecular weight as exemplified by diethylenetriaminetetraacetic acid iron complex salts and 1,3-propylenediaminetetraacetic acid complex salts in place of ethylenediaminetetraacetic acid ferric complex salts. However, as a result of the researches made by the present inventors, these compounds were found to largely form the ferrous complex salts at the high pH. If the ferrous complex salts are present in the bleaching solution or bleach-fixing solution, not only the bleaching performance becomes inferior but also there may occur the difficulties, the so-called poor color recovery that dyes, particularly cyan dyes, are reduced to turn to leuco dyes, thus bringing about fatal disadvantages.

Also, what is preferred in the circulation course that these ferric complex are further synthesized and finally supplied as processing agents for photography is the lightness in weight. However, considering those available in the form of liquid and those available in the form of powder, the form of liquid is more advantageous than the form of powder for simplifying the dissolving operations, when used as the photographic processing agents as mentioned above, and also considering the stage of synthesis, the form of liquid has been desired as it is possible to omit the step of crystallization from reaction mixtures, making it possible to lower the cost. Also in the case of the liquid form, more preferred are those having been concentrated as much as possible when taking account of the circulation, but there may occur serious problems that the more concentrated an aqueous solution of ferric complex salts is, the more readily the poor color recovery may be caused when it is made as a photographic processing solution. As a result of studies made by the present inventors, the ferrous complex salts were found to have been generated, and there has been a strong demand for improvement.

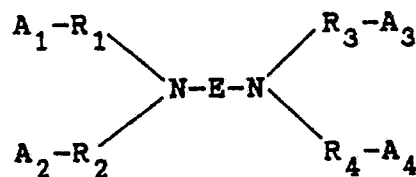
SUMMARY OF THE INVENTION

An object of the present invention is to provide a composition containing a ferric complex salt, that can suppress the generation of ferrous complex salts and be best suited when used in preparing bleaching solutions or bleach-fixing solutions that are free from the poor color recovery and stable over a long period of time.

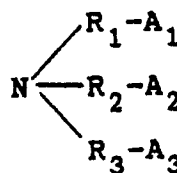
Other objects of the present invention will become apparent from the following description in the present specification.

The above objects of the present invention can be achieved by an aqueous composition containing in water at least 180 g per liter of a ferric complex salt of the compound represented by Formula (I) or (II) shown below, and having the pH of not more than 7.0;

Formula (I)



Formula (II)



wherein E represents a substituted or unsubstituted alkylene group, cycloalkylene group or phenylene group, $-\text{R}_5\text{OR}_5\text{OR}_5-$, or $-\text{R}_5\text{ZR}_5-$; Z represents $\text{>N-R}_5\text{-A}_5$ or >N-R_5 ; R_1 to R_5 each represent a substituted or unsubstituted alkylene group; A_1 to A_5 each represent a hydrogen atom, $-\text{OH}$, $-\text{COOM}$, or $-\text{PO}_3\text{M}_2$; and M represents a hydrogen atom or an alkali metal atom, an ammonium group, a group containing a quaternary ammonium.

The present inventors found a surprising fact that although the ferrous complex salts may readily be generated in a highly concentrated solution of the ferric complex salt of the compound represented by Formula (I) or (II) when the pH is more than 7.0, the generation of ferrous complex salts can be dramatically suppressed by controlling the pH to not more than 7.0.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing the proportion of ferrous complex salt formation with respect to pH obtained in Example 1 described herein.

DETAILED DESCRIPTION OF THE INVENTION

Specific exemplary compounds of the compound represented by Formula (I) or (II) are listed below.

[Exemplary compounds]

- (I-1) Ethylenediaminetetraacetic acid
- (I-2) Diethylenetriaminepentaacetic acid
- (I-3) Ethylenetriamine-N-(β -hydroxyethyl)-N,N',N'-triacetic acid.
- (I-4) 1,3-Propylenediaminetetraacetic acid
- (I-5) Triethylenetetraminehexaacetic acid
- (I-6) Cyclohexenediaminetetraacetic acid
- (I-7) 1,2-Diaminopropanetetraacetic acid
- (I-8) 1,3-Diaminopropan-2-ol-2-tetraacetic acid
- (I-9) Ethyletherdiaminetetraacetic acid
- (I-10) Glycoletherdiaminetetraacetic acid
- (I-12) Ethylenediaminetetrapropionic acid
- (I-12) Phenylenediaminetetraacetic acid
- (I-13) Disodium ethylenediaminetetraacetate
- (I-14) Tetra(trimethylammonium) ethylenediaminetetraacetate
- (I-15) Tetrasodium ethylenediaminetetraacetate
- (I-16) Pentasodium diethylenetriaminepentaacetate
- (I-17) Sodium ethylenetriamine-N-(β -hydroxyethyl)-N,N',N'-triacetate
- (I-18) Sodium propylenediaminetetraacetate
- (I-19) Ethylenediaminetetramethylenephosphonic acid
- (I-20) Sodium cyclohexenediaminetetraacetate
- (I-21) Diethylenetriaminepentamethylenephosphonic acid
- (I-22) Cyclohexenediaminetetramethylenephosphonic acid
- (II-1) Nitrilotriacetic acid

- (II-2) Iminodiacetic acid
- (II-3) Hydroxyethyliminodiacetic acid
- (II-4) Nitrilotripropionic acid
- (II-5) Nitrilotrimethylenephosphonic acid
- 5 (II-6) Iminodimethylenephosphonic acid
- (II-7) Hydroxyethyliminodimethylenephosphonic acid
- (II-8) Sodium nitrilotriacetate

Of the ferric complex salts of these organic acids, the effect of the present invention can be effectively exhibited in respect of the compounds having a large molecular weight, and the molecular weight of the organic acid may preferably be 300 or more.

Of these organic acids, the compounds by which the effect of the present invention can be more preferably exhibited may include diethylenetriaminepentaacetic acid, propylenediaminetetraacetic acid, 1,2-diaminopropanetetraacetic acid, 1,4-diaminobutanetetraacetic acid, glycoetherdiaminetetraacetic acid, and cyclohexanediaminetetraacetic acid, and particularly preferably diethylenetriaminepentaacetic acid and 1,3-propylenediaminetetraacetic acid.

These ferric complex salts may also take the form of free compounds, but in many cases take the form of alkali metal salts such as sodium salts and potassium salts, or ammonium salts and tertiary ammonium salts. However, as the counter salts that can effectively exhibit the effect of the present invention preferably include ammonium salts, and this ammonium salts are also preferable in view of the solubility. These organic acid ferric complex salts according to the present invention are in concentration of 180 g or more per liter of the composition containing the ferric complex salt of the present invention, but, to achieve more effective exhibition of the effect of the present invention, preferably of from 200 g to 700 g, and most preferably of from 210 g to 600 g.

Also, the composition containing the ferric complex salt of the present invention has the pH of 7 or more, but, to achieve more effective exhibition of the effect of the present invention, may preferably have pH 6.5 or less, more preferably pH 2.5 to pH 6.5 from the viewpoint of the solubility, and particularly more preferably pH 4.0 to pH 6.0.

The composition containing the ferric complex salt of the present invention may preferably contain substantially no thiosulfate.

This is because the presence of the thiosulfate generally used in bleach-fixing solutions, together with the organic acid ferric complex salt may result in the generation of a ferrous complex salt during storage for a long period of time, so that there are disadvantages that not only the effect of the present invention can not be effectively exhibited but also the so-called sulfidation that the thiosulfate is oxidized during storage to cause precipitation of sulfur tends to occur in the concurrent presence of the ferric complex salts, undesirably.

Accordingly, when the solution for use is prepared with use of the composition containing the ferric complex salt of the present invention, in the case of the bleaching solution for example, available is a method in which a halogen such as ammonium halide is contained in the composition containing the ferric complex salt of the present invention and the mixture is diluted with water as it is, to prepare the solution for use, or a method in which the bleaching solution is divided into two parts, namely, the composition (part) containing the ferric complex salt of the present invention and a composition (part) of an alkali such as ammonium and alkali carbonates are made ready for use, and both are mixed to prepare the bleaching solution (solution for use). In the case of the bleach-fixing solution, available is a method in which it is divided into the composition (part) containing the ferric complex salt of the present invention, corresponding to a beaching component, and a composition (part) containing thiosulfate, and, after mixing and dilution, the pH of the composition (part) containing thiosulfate is set so as to be the pH preferred as the solution for use. Also available is a method in which the bleach-fixing solution is divided into three parts to give the composition (part) containing the ferric complex salt of the present invention, a composition (part) containing thiosulfate and a composition (part) containing alkali agents such as ammonia water and alkali carbonates.

The composition containing the ferric complex salt of the present invention can be optimally used over the whole light-sensitive silver halide photographic materials that require the bleach or bleach-fixing processing. However, uses of the composition containing the ferric complex salt of the present invention may not be limited to this, and it can be used over the whole uses of the compositions containing ferric complex salts for which the generation of ferrous complex salts during storage is desired to be suppressed. For example, they include the uses as bleaching agents in the field of fiber industries, etc., and other uses.

In instances in which the composition containing the ferric complex salt of the present invention is used as a photographic processing solution, or a kit or parts thereof, there may be paid no regard as to the type of light-sensitive silver halide photographic materials to be processed, the manner by which emulsions are

prepared, the type of couplers, and the type of sensitizers and other photographic additives.

In instances in which the composition containing the ferric complex salt of the present invention is used in combination with other compositions, there may also be paid no regard as to whether the compositions to be used in combination is in the form of liquid (including concentrated ones) or powder. These may be further paid no regard as to containers for storing the composition containing the ferric complex salt of the present invention, whether they are made of glass, plastics or something else, and it may be placed in a container serving also as a processing tank.

EXAMPLES

Examples of the present invention will be described below, but the present invention is by no means limited to these.

Example 1

Organic acid ferric complex salts shown below were each dissolved in amount of 120 g per 500 ml of water, and the solutions were each adjusted to have the pH to range from 4 to 10 and put into a polyethylene container, which was left to stand for 2 weeks at 50° C to thereafter determine the concentration to each organic acid ferrous complex salt in said composition (processing agent kit) according to an o-phenanthroline method. Results are shown in Fig. 1.

- (1) Ethylenediaminetetraacetic acid iron (III) ammonium dihydrate
- (2) Diethylenetriaminepentaacetic acid iron (III) diammonium monohydrate
- (3) 1,3-Propylenediaminetetraacetic acid iron (III) ammonium
- (4) 1,2-Diaminopropanetetraacetic acid iron (III) ammonium
- (5) Hydroxyethyliminodiacetic acid iron (III)

As shown in Fig. 1, in the organic acid iron (III) complex salts, the formation of ferrous complex salt can be suppressed when the pH is controlled to 7 or less.

Similar effects were also confirmed to be obtainable also in respect of cyclohexanediaminetetraacetic acid iron (III) complex salts and glycoetherdiaminetetraacetic acid iron (III) complex salts.

Example 2

Using the compositions (iron salt solutions) used in Example 1, having been stored and having the respective pH, 150 g of ammonium bromide were added thereto, and the respective mixtures were diluted to 1 liter, adjusting the pH to 6.0, to prepare bleaching solutions. Using these bleaching solutions, processing was carried out according to the processing steps shown below and using samples obtained by subjecting the light-sensitive materials shown below, to measure maximum density of cyan dyes having been processed. Thereafter, the samples were dipped for 6 minutes and 30 seconds in the re-oxidizing solution shown below to measure the (difference between cyan maximum density before re-oxidation and cyan maximum density after re-oxidation). Results obtained are shown in Table 1.

[Processing steps]

	<u>Time</u>	<u>Temperature</u>
5 Color developing	3 min 15 sec	38°C
Bleaching	3 min 15 sec	38°C
10 Fixing	3 min 15 sec	35°C
Washing	3 min	30 to 34°C
Stabilizing	1 min 20 sec	30 to 34°C
15 Drying		

The following were used as a color developing solution, a fixing solution and a stabilizing solution.

[Color developing solution]

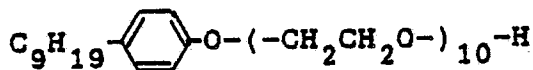
25 Potassium carbonate 30.0 g
 Sodium sulfite 2.0 g
 Hydroxylamine sulfate 2.0 g
 Potassium bromide 1.2 g
 Sodium hydroxide 3.4 g
 30 3-Methyl-4-amino-ethyl-N-β-hydroxyethyl-aniline sulfate 4.6 g
 Made up to 1 liter by adding water, and adjusted to pH 10.1 using sodium hydroxide and 50 % sulfuric acid.

[Fixing solution]

35 Aqueous ammonium thiosulfate solution (72.5 %) 250 ml
 Ammonium sulfite 20 g
 40 Made up to 1 liter by adding water, and adjusted to pH 7.0 using ammonia and acetic acid.

[Stabilizing solution]

45 Formalin (an aqueous 30 % solution) 7.0 ml



50 1.0 ml
 Made up to 1 liter by adding water.

55

[Re-oxidizing solution]

Ethylenediaminetetraacetic acid iron (III) ammonium 100g
Made up to 1 liter using water, and adjusted to pH 6.0 using ammonia water.

5

Light-sensitive materials:

On a triacetate film base, provided were a halation-preventive layer and a gelatin layer, on which coated
10 were a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a filter layer
containing yellow colloid silver and a blue-sensitive silver halide emulsion layer so as to give total silver
amount of 62 mg per 100 cm². The above emulsion layers comprised silver iodobromide whose mol % of
silver iodide was 4.8 %. In this occasion, used in the blue-sensitive silver halide emulsion layer was α -(4-
nitrophenoxy)- α -pivalyl-5-(γ -(2,4-di-t-aminophenoxy)butylamido)-2-chloroacetoanilide as an yellow coupler,
15 used in the green-sensitive silver halide emulsion layer were 1-(2,4,6-trichlorophenyl)-3-{[α -2,4-di-t-amyl-
phenoxy]acetamido]benzamido}-3-pyrazolone and 1-(2,4,6-trichlorophenyl)-3-{[α -2,4-di-t-amylphenoxy]-
acetamido]benzamido}-4-(4-methoxyphenylazo)-5-pyrazolone as magenta couplers, and used in the red-
sensitive silver halide emulsion layer was the following (C-1) as a cyan coupler. To the respective emulsion
layers, usual additives such as sensitizing dyes and hardening agents were respectively added according to
20 conventional methods.

Cyan coupler (C-1):

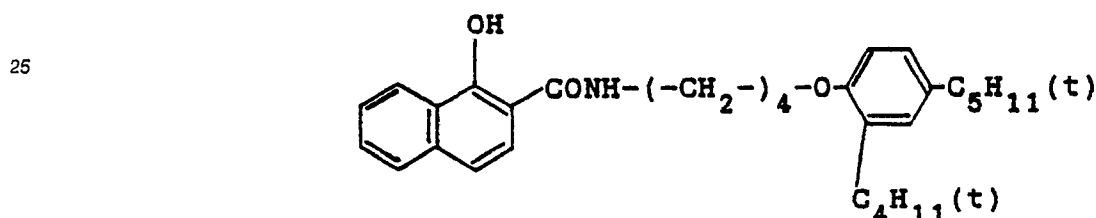


Table 1

35

Compo- sition No.	pH in Compositions							
	2.5	4	5	6	6.5	7	8	9
(1)	0.04	0.04	0.05	0.05	0.05	0.06	0.10	0.14
(2)	0.01	0.01	0.01	0.02	0.03	0.05	0.20	0.35
(3)	0.04	0.04	0.04	0.05	0.06	0.10	0.60	0.62
(4)	0.02	0.02	0.03	0.03	0.03	0.04	0.08	0.12
(5)	0.10	0.12	0.13	0.15	0.16	0.17	0.25	0.32

50

As shown in the above Table 1, the degree of poor color recovery becomes smaller by controlling the
pH to 7 or less when the compound of the present invention is used, showing good results, and particularly
great effect can be obtained in the cases of diethylenetriaminetetraacetic acid and 1,3-
diqaminopropanetetraacetic acid.

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Example 3

Storage was made in the same manner as in Example 1 in the state that 150 g each of ammonium bromide were added in each of the compositions shown in Example 1, and the concentration of ferrous complex salts was measured to obtain substantially the same results as in Example 1.

This composition was also diluted to 1 liter and adjusted to have the pH of 6.0 using ammonia water or acetic acid, to measure the degree of poor color recovery in the same manner as in Example 2. As a result, there were obtained the results similar to those in Example 2.

Example 4

In each of the compositions of Example 1, added were 250 ml of ammonium thiosulfate (72.5 %) solution, 10 g of sodium sulfite and 1 g of 2-amino-5-mercapto-1,3,4-thiadizole, and the mixture was diluted to 1,000 ml using water and the resulting solution was adjusted to pH 7.0 using ammonia water or acetic acid, thus preparing bleach-fixing solutions, which were subjected to the processing according to the following processing steps.

	<u>Time</u>	<u>Temperature</u>
Color developing	3 min 15 sec	38°C
Bleach-fixing	3 min 15 sec	38°C
Washing	3 min	30 to 34°C
Stabilizing	1 min 20 sec	30 to 34°C
Drying		

Using those same as in Example 1 in respect of other processing solutions and light-sensitive material samples, the poor color recovery at the maximum density of cyan dyes was measured in the same manner. Results obtained are shown in Table 2.

Table 2

Compo- sition No.	pH in Compositions							
	2.5	4	5	6	6.5	7	8	9
(1)	0.04	0.04	0.04	0.06	0.06	0.08	0.16	0.20
(2)	0.03	0.03	0.02	0.03	0.04	0.10	0.41	0.46
(3)	0.01	0.01	0.02	0.01	0.01	0.02	0.56	0.63
(4)	0.01	0.01	0.02	0.02	0.02	0.03	0.18	0.22
(5)	0.09	0.10	0.14	0.14	0.14	0.16	0.27	0.38

As will be clear in the above Table 2, in the bleach-fixing solutions also, the degree of poor color

recovery becomes smaller by controlling the pH to 7 or less like the case of the bleaching solution of Example 2, showing good results.

5 Example 5

In each of the compositions (processing agent kits) of Example 1, added were 250 ml of ammonium thiosulfate (72.5 %) solution and 10 g/lit of sodium sulfite, and the resulting solutions were each made up to 500 ml in the same manner as in Example 1, which were stored in the same manner as in Example 1 to
10 measure the formation amount of ferrous ions after storage, and the proportion thereof was calculated to obtain the results as shown in Table 3.

Table 3

15

Compo- sition No.	pH in Compositions							
	2.5	4	5	6	6.5	7	8	9
20 (1)	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	42%	44%
(2)	Sfdz	Sfdz	Sfdz	35%	40%	48%	80%	100%
(3)	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	100%
25 (4)	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	46%	52%
(5)	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	Sfdz	100%

30

Sfdz: sulfidized

As will be clear from the above Table 3, mixing thiosulfate in the compositions, the so-called sulfidation that the thiosulfate react with bleaching agents because of storage to undergo decomposition to cause
35 precipitation of sulfur tends to occur, which is particularly remarkable at a lower pH. Ferrous complexes also are violently generated at a higher pH, in any case resulting in a greater deterioration during storage.

Example 6

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In respect of (2) and (3) in Example 1, the volume 120 g (kit volume) of each iron complex salt in the compositions was varied as shown in Table 4 below to examine the generating proportion of generated ferrous ions in the same manner as in Example 1. Results obtained are shown in Table 4.

45

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Table 4

Com- posi- tion No.	pH	Volume of compositions (ml)					
		250	400	571	600	667	800
		Iron concentration in compositions (g/lit)					
		480	300	210	200	180	150
	4	1(%)	1(%)	1(%)	1(%)	1(%)	1(%)
	5	1	1	1	1	1	2
	6	2	2	2	2	2	2
(2)	7	4	4	3	3	2	2
	8	30	28	25	20	18	5
	9	58	57	50	46	38	8
	10	94	93	90	80	49	12
	4	5	4	4	4	4	4
	5	7	7	7	7	6	6
	6	13	13	12	12	10	11
(3)	7	33	32	30	30	25	24
	8	100	100	98	95	95	37
	9	100	100	100	100	100	48
	10	100	100	100	100	100	60

As will be clear from the above Table 4, the effect of the present invention is effectively exhibited when the organic acid ferric complex salt is contained in the composition in concentration of 180 g per liter of the composition, and is particularly remarkable when it is 210 g or more.

Example 7

Prepared were 200 lit. each of solutions in which the iron complex salt in each of (2) and (3) in Example 1 was varied in its concentration and dissolved, which were enclosed in steel drums and left to stand for 1 month at room temperature (25°C) to examine the generating proportion of ferrous irons generated after they were left to stand. Results obtained are shown in Table 5.

Table 5

Com- posi- tion No.	pH	Iron concentration in compositions (g/lit)						
		600	480	300	210	200	180	150
	4	1 (%)	1 (%)	1 (%)	1 (%)	1 (%)	1 (%)	1 (%)
	5	1	1	1	1	1	1	2
	6	2	2	2	2	2	2	2
(2)	7	4	4	4	3	3	2	2
	8	30	29	23	20	16	14	3
	9	48	40	36	30	26	24	5
	10	87	82	78	72	50	30	8
	4	5	4	3	3	3	3	3
	5	7	6	6	5	5	4	4
	6	13	11	10	8	8	6	5
(3)	7	35	24	20	18	15	14	12
	8	100	96	94	82	80	80	30
	9	100	100	100	100	100	100	40
	10	100	100	100	100	100	100	48

40

As shown in the above Table 5, the ferrous complex salts are generated in a large proportion when the ferrous complex salts are used in a higher concentration, but it was found that the generation of ferrous complex salts was suppressed when the pH is in the range of the present invention, and the effect of the present invention is also remarkable in the instances where the compositions containing the ferric complex salts are used in a large quantity.

45

Example 8

50

Using the processing solutions same as those in Example 2, processing was carried out using the samples same as those in Example 2.

Provided that in place of washing, used were a washing-free stabilizing solution and an alkali stabilizing solution that have the make-up shown below. As a result, there were obtained the results similar to those as in Example 2.

55

[Washing-free stabilizing solution]

5-Chloro-2-methyl-4-isothiazolin-3-on 0.01 g

2-Methyl-4-isothiazolin-3-on 0.01 g

5 Ethylene glycol 2.0 g

Made up to 1 liter using water, and adjusted to pH 7.0 using ammonia water and sulfuric acid.

10 [Alkali stabilizing solution]

Potassium carbonate 10 g

Diethylenetriaminepentaacetic acid iron (II) complex 5 g

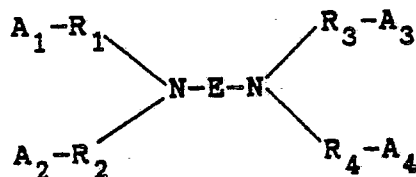
Diethylenetriaminepentaacetic acid 2 g

15 Made up to 1 liter using waster and adjusted the pH of the solution at 10.0.

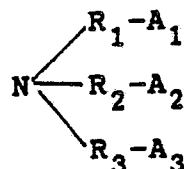
Claims

- 20 1. An aqueous composition comprising at least 180 g per liter of a ferric complex salt of the compound represented by formula (I) or (II) shown below, and having the pH of not more than 7.0;

Formula (I)



Formula (II)



40 wherein E represents a substituted or unsubstituted alkylene group, cycloalkylene group or phenylene group, a $-R_5OR_5OR_5-$ group, or a $-R_5ZR_5-$ group; Z represents a $\text{>N-R}_5\text{-A}_5$ group or a >N-R_5 group; R_1 , R_2 , R_3 , R_4 and R_5 independently represent a substituted or unsubstituted alkylene group; A_1 , A_2 , A_3 , A_4 and A_5 independently represent a hydrogen atom, -OH, a -COOM group, or a $-\text{PO}_3\text{M}_2$ group; and M represents a hydrogen atom, an alkali metal atom, an ammonium group or a group containing a quaternary ammonium.

45 2. The aqueous composition of claim 1, wherein said compound of formula (I) or (II) has a molecular weight of not less than 300.

3. The aqueous composition of claim 1 or 2, wherein at least one of A_1 , A_2 , A_3 , A_4 and A_5 is -OH, a -COOM group or a $-\text{PO}_3\text{M}_2$ group; and M represents a hydrogen atom, an alkali metal atom, an ammonium group or a group containing a quaternary ammonium.

4. The aqueous composition of claim 1, 2 or 3, wherein said ferric complex compound is an ammonium salt.

5. The aqueous composition of claim 1, 2, 3 or 4, wherein said ferric complex compound is contained in a quantity of 200 g to 700 g per liter of the composition.

55 6. The aqueous composition of claim 5, wherein the quantity is 210 g to 600 g per liter of the composition.

7. The aqueous composition of claims 1 or 2 to 6, wherein the pH of the composition is not more than 6.5.

8. The aqueous composition of claim 7, wherein the pH of the composition is 2.5 to 6.5

9. The aqueous composition of claim 8, wherein the pH of the composition is 4.0 to 6.0

10. The aqueous composition of claims 1 or 2 to 9, wherein compound of formula (I) or (II) is selected from the group consisting of (I-1) to (II-8);

(I-1) Ethylenediaminetetraacetic acid

(I-2) Diethylenetriaminepentaacetic acid

(I-3) Ethylenetriamine-N-(β -hydroxyethyl)-N,N',N'-triacetic acid

(I-4) 1,3-Propylenediaminetetraacetic acid

(I-5) Triethylenetetraminehexaacetic acid

(I-6) Cyclohexenediaminetetraacetic acid

(I-7) 1,2-Diaminopropanetetraacetic acid

(I-8) 1,3-Diaminopropan-2-ol-2-tetraacetic acid

(I-9) Ethyletherdiaminetetraacetic acid

(I-10) Glycoletherdiaminetetraacetic acid

(I-12) Ethylenediaminetetrapropionic acid

(I-12) Phenylenediaminetetraacetic acid

(I-13) Disodium ethylenediaminetetraacetate

(I-14) Tetra(trimethylammonium) ethylenediaminetetraacetate

(I-15) Tetrasodium ethylenediaminetetraacetate

(I-16) Pentasodium diethylenetriaminepentaacetate

(I-17) Sodium ethylenetriamine-N-(β -hydroxyethyl)-N,N',N'-triacetate

(I-18) Sodium propylenediaminetetraacetate

(I-19) Ethylenediaminetetramethylenephosphonic acid

(I-20) Sodium cyclohexenediaminetetraacetate

(I-21) Diethylenetriaminepentamethylenephosphonic acid

(I-22) Cyclohexenediaminetetramethylenephosphonic acid

(II-1) Nitrilotriacetic acid

(II-2) Iminodiacetic acid

(II-3) Hydroxyethyliminodiacetic acid

(II-4) Nitrilotripropionic acid

(II-5) Nitrilotrimethylenephosphonic acid

(II-6) Iminodimethylenephosphonic acid

(II-7) Hydroxyethyliminodimethylenephosphonic acid

(II-8) Sodium nitrilotriacetate

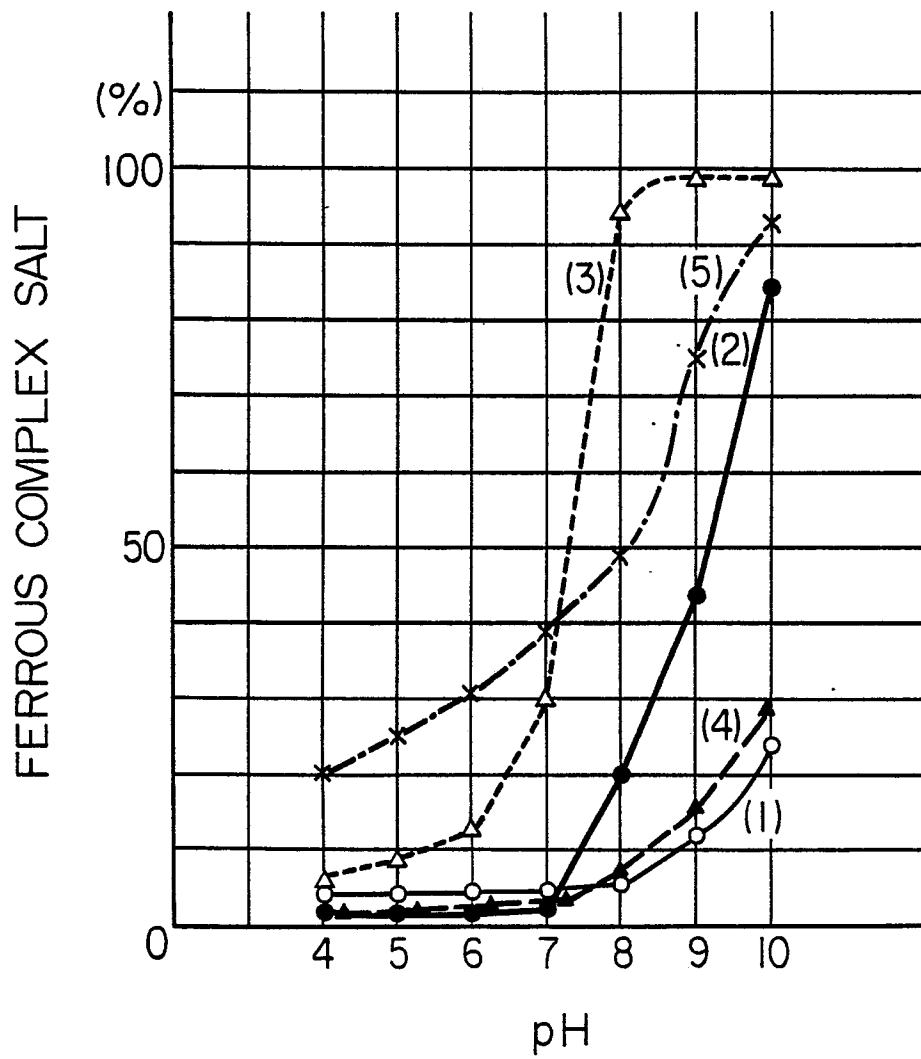
11. The aqueous composition of claim 10, wherein said compound is selected from the group consisting of diethylenetriaminepentaacetic acid or an alkali metal salt or an ammonium salt thereof; propylenediaminetetraacetic acid or an alkali metal salt or an ammonium salt thereof; 1,2-diaminopropanetetraacetic acid or an alkali metal salt or an ammonium salt thereof; 1,4-diaminobutanetetraacetic acid or an alkali metal salt or an ammonium salt thereof; glycoletherdiaminetetraacetic acid or an alkali metal salt or an ammonium salt thereof; and cyclohexanediaminetetraacetic acid or an alkali metal salt or an ammonium salt thereof.

12. The aqueous composition of claim 10, wherein said compound is diethylenetriaminepentaacetic acid or an alkali metal salt or an ammonium salt thereof or 1,3-propylenediaminetetraacetic acid or an alkali metal salt or an ammonium salt thereof.

13. The aqueous composition of claims 1 or 2 to 12, wherein said composition is substantially free of thiosulfate.

Not eingereicht / Nowly filed
Nouvellement déposé

FIG. 1





EP 88 10 8310

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. 4)
X	EP-A-0 158 369 (KONISHIROKU PHOTO IND., CO.) * Page 5, lines 4-13; pages 8-15; page 24, lines 10-17 *	1-13	G 03 C 7/42 G 03 C 5/26
A	GB-A- 748 494 (HAUFF AG) * Page 2, lines 52-63 *	1-13	
A	EP-A-0 197 437 (KONISHIROKU PHOTO IND., CO.) * Page 25, line 10 - page 26, line 5 *	1-13	
A	EP-A-0 219 113 (FUJI PHOTO FILM CO.) * Page 7, line 18 - page 8, line 22 *	1-13	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			G 03 C 7/00 G 03 C 5/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16-09-1988	Examiner MAGRIZOS S.
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			