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[54] **COMPOSITION FOR PROCESSING SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE ELEMENTS**

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[52] **U.S. Cl.** ..... **96/66 R,** 96/66.4

[51] **Int. Cl.** **G03c 5/30**

[58] **Field of Search** 46/60, 61, 50, 66, 62, 46/63, 65, 66

[56] **References Cited**

UNITED STATES PATENTS

3,189,454	7/1965	Luckey et al.	96/61 R
3,586,631	6/1971	Fassbender	96/50
3,634,088	1/1972	Cooley	96/50
3,658,535	4/1972	Willems	96/60
3,467,521	9/1969	Frank	96/66.2

OTHER PUBLICATIONS

Chaberek & Martell, "Organic Sequestering Agents," 1959, p. 156.

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[57] **ABSTRACT**

Composition for processing a silver halide photographic light-sensitive element containing ethylenebis(β-oxyethylamine) tetraacetic acid or its alkali salt. The compound has a calcium ion-chelating or masking ability superior to that of EDTA.

9 Claims, No Drawings

COMPOSITION FOR PROCESSING SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE ELEMENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a processing composition for use in processing a silver halide photographic light-sensitive element. More particularly, the invention is concerned with such a processing composition containing a chelating agent for the calcium ion present in a solvent used for dissolution of said photographic processing composition.

2. Description of the Prior Art

A silver image is, in general, formed after exposure of a silver halide photographic light-sensitive element by development and fixing, which may be combined with other optional processings such as bleaching, hardening, stopping or stabilizing. In effecting these processings, the processing agents used in each processing are generally used as an aqueous solution, so that the properties of each processing composition vary largely with the quality of the water used. For instance, water which contains a high calcium ion content, i.e., so called hard water, reacts with carbonates, sulfites, borates or like salts present in the processing agents to form water-insoluble calcium salts. Such calcium salts adhere to the photographic light-sensitive element to be processed (this is called the production of scum), and the solidified calcium salts may injure the emulsion layer of the photographic light-sensitive element. Furthermore, the calcium salts may be deposited in the processing apparatus, ultimately causing breakdown of the apparatus.

In an attempt to eliminate such defects, it has been proposed to mask the calcium ion, and, as the calcium masking agent there is known a polyphosphate such as sodium tetrapolyphosphate, aminopolyacetic acid or a salt thereof, ethylene diamine tetraacetic acid or a salt thereof, and the like.

These known calcium masking agents are, however, all insufficient to be used in photographic processing compositions. For instance, although the polyphosphate has an excellent masking ability, the ability is reduced when used in an alkaline processing composition due to conversion of the polyphosphate to orthophosphate.

Ethylene diamine tetraacetic acid (EDTA) or its alkali salt is at present considered the most excellent calcium masking agent, but, when added to a processing composition containing an organic reducing agent such as a developing agent, it will accelerate the oxidation of the organic reducing agent such as a developing agent, thereby reducing the stability thereof. Such a phenomenon is in particular prominent when iron is present in the processing composition.

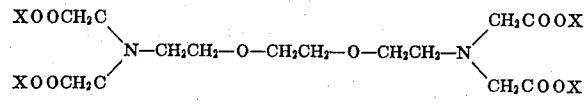
SUMMARY OF THE INVENTION

One object of the present invention is to provide a composition of processing agents for use in processing a silver halide photographic light-sensitive element, which composition possesses both excellent calcium masking and stability.

This object can be accomplished by adding at least one of ethylenebis(β-oxyethylamine)-tetraacetic acid

or its alkali metal salt into the processing agent composition.

The ethylenebis(β-oxyethylamine) tetraacetic acid or its alkali metal salt is represented by the following general formula:



wherein X stands for a hydrogen atom or an alkali metal atom such as sodium or potassium.

DETAILED DESCRIPTION OF THE INVENTION

Since the above-described compound is in the form of a powder, it may be added directly into a processing solution, or added prior to the preparation of the processing solution to the processing agents in the form of a powder. Accordingly, as herein used, the term "composition of processing agents" includes the processing agents in the form of both liquid and powder.

The calcium masking agents according to the present invention show in particular remarkable effect when added into a composition of photographic processing agents containing an organic reducing substance such as a developing agent, although they may be added into any composition of photographic processing agents which contains calcium ions, for example, hard water. Such compositions of processing agents include fixing solutions, bleaching solutions, hardening solutions, stopping solutions and stabilizing solutions. Formulation of each composition of processing agents is in no way limited so far as the composition has its function, because the effect of the compounds of the invention is basically connected with the calcium-containing water itself. Although the fore-going description of the invention has been made with particular reference to the calcium-containing water, it will be apparent that the same effect is encountered when other liquids containing calcium ions are used as a solvent for the processing agents.

The amount of the compound according to the invention is in the range of from 0.1 to 10, preferably from 0.5 to 3 g. per liter of photographic processing solution.

The present composition of photographic processing agents as herein described and hereinafter claimed may be applied to solutions for processing black and white photographic light-sensitive elements including X-ray films, lith-films, microfilms, printing paper and the like, and color photographic light-sensitive elements.

The present invention will be further explained by the following examples.

Example 1

As the auto-developer for a direct X-ray film for medical use there was prepared a liquid composition of the following formulation.

Formulation of developer

Anhydrous sodium sulfite	40.0 g.
Hydryquinone	30.0 g.
1-phenyl-3-pyrazolidone	1.5 g.
Potassium hydroxide	22.0 g.
Anhydrous potassium carbonate	15.0 g.

-Continued

Formulation of developer	
Glutaraldehyde	6.0 g.
Potassium bromide	4.0 g.
1-phenyl-5-mercaptotetrazole	0.1 g.
Water to make 1 liter	

This developer is hereinafter referred to as Developer A. Into the Developer A there was added 2.7×10^{-3} mole ethylenebis(β-oxyethylamine) tetraacetic acid to prepare Developer B, while into the Developer A was added 2.7×10^{-3} mole EDTA to prepare Developer C. The amount of calcium carbonate which could be dissolved in the respective Developers A to C was as follows.

Developer	Amount of calcium carbonate dissolved
A	0.03 g.
B	0.36 g.
C	0.12 g.

As is evident from the results, the calcium ions can be masked by the Developer B according to the present invention and the affect of calcium ions can be reduced to one third that in the Developer C containing EDTA.

Example 2

Using Developers A to C in Example 1, the difference in hydroquinone-oxidation velocity between the case of solutions containing a low iron ion content and the case of a high iron ion content was investigated. The oxidation of hydroquinone was carried out under the same conditions in every case by air-oxidation. The air-oxidation was effected at room temperature using vessels in which the surface area of the developer surface in contact with air and the volume of the developer were identical in every case, thereby effecting a natural air-oxidation. The results are shown in the following table.

Developer	Amount of oxidized hydroquinone (g./l) In the absence of iron ions	In the presence of 20 mg./l of iron ions
A	10.1	12.1
B	10.5	10.3
C	17.0	21.6

As is evident from the above results, oxidation occurs with more difficulty in the case of the developer according to the present invention in comparison with the developer containing EDTA, even in the presence of iron ions.

Example 3

Each of Developers A to C was oxidized for a given period of time, and using the resulting developers, a direct X-ray film for medical use was developed. The various photographic properties of the film are shown in the following table. In each of Developers A to C there was contained about 0.1 mg/liter of iron ions. The oxidation of these Developers was carried out according to the method described in Example 2. The exposure, development, measurement of photographic density and the like were all effected in a conventional manner, using the same conditions in every case.

Properties	Developer A	Developer B	Developer C
Fog	0.06	0.06	0.04
Relative speed at fog-density plus 1.0 photographic density	100	98	51
Maximum density ($D_{max.}$)	3.30	3.45	3.00
Contrast	2.30	3.45	3.00

Example 4

Ammonium thiosulfate	150.0 g.
Anhydrous sodium sulfite	15.0 g.
Boric acid	10.0 g.
Acetic acid (90% aqueous solution)	23.0 c.c.
Anhydrous aluminum sulfate	9.0 g.
Water to make 1 liter	

Into a fixing solution of the above-described formulation there was dissolved calcium carbonate and white turbidity was observed at a concentration of 4 g/l calcium carbonate. When 4 g/l of calcium carbonate was added into a fixing solution having added thereinto 2.7×10^{-3} mole of ethylenebis(β-oxyethylamine)tetraacetic acid, no white turbidity was observed, which clearly shows the fact that the ethylenebis(β-oxyethylamine) tetraacetic acid has a calcium ion masking effect in fixing solutions.

Example 5

As the developer for a color-photographic light-sensitive element there was prepared a developer of the following formulation into which was incorporated 1 mg/l of iron ions. The resulting developer is hereinafter referred to as Developer D. Into Developer D there was added 3.0×10^{-3} mole of ethylenebis(β-oxyethylamine)-tetraacetic acid to prepare Developer E, or 3.0×10^{-3} mole of EDTA to prepare Developer F.

Formulation of Developer D	
Para-amino-N,N-diethylaniline sulfate	2.0 g.
Anhydrous sodium sulfite	2.0 g.
Sodium carbonate monohydrate	60.0 g.
Hydroxylamine hydrochloride	0.5 g.
Potassium bromide	0.4 g.
Water to make 1 liter	

After oxidizing each of Developers D to F for a given time by the method described in Example 2, the amount of the developing agent oxidized thereby was determined, the results being shown in the following table.

Developer	The amount of the developing agent oxidized
D	0.34 g.
E	0.44 g.
F	1.5 g.

As is evident from the above-described table, prevention of developing agent oxidation by means of the compound of the invention is superior to that by using EDTA.

This invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereabove and as defined in the appended claims.

What is claimed is:

1. A developing composition comprising a black and white or color silver halide developing agent and a sequestering agent, wherein the improvement comprises said sequestering agent being at least one of ethylene bis(beta-oxyethylamine)tetraacetic acid and its alkali metal salts at a level such that when a developing solution is formed from said composition, said ethylene bis-(beta-oxyethylamine)tetraacetic acid or its alkali metal salts are present at a level of from 0.1 to 10 g. per liter of said developing solution.

2. A developing composition as claimed in claim **1**, wherein said alkali metal salt is a sodium or potassium salt.

3. A developing composition as claimed in claim **1** which is in the form of a powder.

4. A developing composition as claimed in claim **1** which is in the form of a liquid.

5. A developing composition as claimed in claim **1** wherein said solution is an aqueous solution.

6. A developing composition as claimed in claim **1**, wherein said developing agent is a hydroquinone or a phenylene diamine developing agent.

7. A method for preventing the air oxidation of an aqueous photographic developing composition containing a black and white or color developing agent for an exposed silver halide element by the addition of a sequestering agent thereto, wherein the improvement comprises adding as the sequestering agent at least one of ethylene bis(beta-oxyethylamine)tetraacetic acid or its alkali metal salts in said developing composition at a level of from 0.1 to 10 g. per liter of said developing solution.

8. A method as claimed in claim **7** wherein said developing agent is a hydroquinone or a phenylene diamine developing agent.

9. A method as claimed in claim **7** wherein said aqueous solution contains iron ions.

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