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TREATMENT OF AND DEVELOPING COMPOSITION FOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIALS

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ABSTRACT OF THE DISCLOSURE

Photographic light sensitive developing compositions containing inositolpolyphosphoric acid or an alkali metal salt of inositolpolyphosphoric acid to prevent staining and aerial fog are disclosed.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a method of treatment of a photographic light-sensitive material, in particular, by the use of an improved developer.

Prior art

It is well known that when a photographic light-sensitive material is treated with a developing solution containing a heavy metal ion, for example, an iron ion or a copper ion, stains often occur. This is caused by many factors, for example, coloring by the reaction product of such heavy metal ion contained in a developer with a photographic light-sensitive material, dyeing of a photographic light-sensitive material with the heavy metal ion itself and catalytic acceleration of aerial fog by the heavy metal ion. The contamination of a developer with heavy metal ions is mainly due to impurities from the water, the processing apparatus and the chemicals used. It is also known that a developing solution prepared from water containing large amounts of calcium ion and magnesium ion, for example, present in hard water, tends to cause turbidity or precipitation.

It has been proposed, as is well known, in order to prevent such staining or precipitation to add to a developing solution a chelating agent such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), 1,3-diamino-2-propanoltetraacetic acid as disclosed in United States Pat. 2,875,049, or condensed polyphosphoric acid, for example, as sold under the trade name of Calgon. However, this attempt is unsatisfactory because although the addition of the known chelating agents to a developer results in a softening of hard water, the addition does not prevent stains. Furthermore, some of these chelating agents accelerate catalytically the oxidation of a developing agent thus shortening the life of the developing solution (see Photographic Science and Engineering 3, 49 (1959)), and accordingly, the use of chelating agents is limited considerably.

It is further well known, on the other hand, that a color developer containing, for example, N,N-diethyl-p-phenylenediamine or N,N-diethyl-2-methyl-p-phenylenediamine, suffers deterioration and aerial fog often is encountered, since a large amount of sulfite cannot be added thereto. Such deterioration or aerial fog can be considerably reduced by adding an antioxidant such as hydroxylamine to a developer but not completely eliminated. In addition, the use of a large amount of an antioxidant such as hydroxylamine rather deteriorates the photographic properties.

It is a principal object of this invention to provide a method of treating a photographic light-sensitive material whereby the above mentioned disadvantages such as staining and fog formation can be overcome.

DESCRIPTION OF THE INVENTION

A compound having very effective chelating properties to prevent stains formed during developing as well as very effective aerial fog inhibiting properties without being harmful to photographic light-sensitive materials and developers over a wide range of addition amounts was sought. It was found that the foregoing object can be accomplished by adding an inositolpolyphosphoric acid or its alkali metal salt to a developing solution. The inositolpolyphosphoric acid or its alkali metal salt used in this invention, being stable, is also effective as hard water softeners and preservatives.

DETAILED DESCRIPTION OF THE INVENTION

Addition of an inositolpolyphosphoric acid or its alkali metal salt to a developing solution according to this invention results in the following advantages:

(1) Staining due to heavy metal ion
(2) Aerial fog
(3) Aerial fog due to the catalytic effect of heavy metal ion
(4) Hard water softening
(5) Preservation of developer

Illustrative of the inositolpolyphosphoric acids or their alkali metal salts used in this invention are the following compounds:

Compound 1.—Inositolhexaphosphoric acid
Compound 2.—Inositolpentaphosphoric acid
Compound 3.—Inositoltetraphosphoric acid
Compound 4.—9Na Inositolhexaphosphate
Compound 5.—11Na Inositolhexaphosphate
Compound 6.—7K Inositolhexaphosphate

The inositolpolyphosphoric acid or its alkali metal salt used in this invention can be synthesized in a conventional manner, for example, as disclosed in Chemical Engineering, Jan. 27, 1958, p. 61.

The compound of this invention is added in a proportion of from 10 mg. to 10 g. for each 1000 ml. of a developing solution. Preferably from 0.1 to 3 g. is used.

The inositolpolyphosphoric acid or its alkali metal salt of the invention can be used together with the above described known compounds.

A developing solution containing the additive of this invention is applicable to any photographic light-sensitive materials, in particular, color photographic light-sensitive materials, in particular, color photographic light-sensitive materials, containing the yellow coupler described in United States Pat. 3,409,439 and British Pat. No. 1,113,038, the magenta coupler described in United States Pat. 3,337,344 and British Pat. No. 1,142,553 and the cyan coupler described in United States Pats. 2,423,730, 2,474,-293, and 2,801,171 and the light-sensitive material described in French Pat. No. 1,576,417.

Typical examples wherein the inositolpolyphosphoric acid or its alkali metal salt of this invention is added to a developing solution are given in the following examples in order to illustrate the invention without limiting the invention.

EXAMPLE 1

A color photographic printing paper having, on a baryta paper as a support, a blue-sensitive silver iodobro-

mide emulsion layer containing benzoylaceto-2-chloro-5-dodecyloxycarbonylanilide as a yellow coupler, a gelatin intermediate layers, a green-sensitive silver chlorobromide emulsion layer containing 1-phenyl-3-[3-(N-butylcapryl-amidepropionamide)]-5-pyrazolone as a magenta coupler, a gelatin intermediate layer, a red-sensitive silver chlorobromide emulsion layer containing 1-hydroxy-2-[3'-(2'', 4''-di-t-amyl-phenoxy)propyl]naphthamide as a cyan coupler and a gelatin protective layer was treated with the developing solution described in The British Journal of Photography, Sept. 27, 1968, p. 838, while adding the compound of the invention or ferric sulfate for a comparison of the stain inhibiting property thereto, at 30° C. for 7 minutes.

Developer-1 (Control):	(pH 10.6)
Sodium metaborate ---------- g	25.0
Sodium sulfite ---------- g	2.0
Hydroxylamine (sulfate) ---------- g	2.0
Potassium bromide ---------- g	0.5
6 - nitrobenzimidazole (nitrate) ---------- g	0.02
Caustic soda ---------- g	4.0
Benzyl alcohol ---------- ml	15.8
Diethylene glycol ---------- ml	20.0
N - ethyl - N - beta - methanesulfonamidoethyl-p - phenylenediamine (sulfate) ---------- g	8.0
Water to 1000 ml.	

Developer-2: 0.1 g. of ferric sulfate was added to 1000 ml. of Developer-1.

Developer-3: 0.1 g. of ferric sulfate and 2 g. of Calgon (trade name) were added to 1000 ml. of Developer-1.

Developer-4: 0.1 g. of ferric sulfate and 2 g. of EDTA-2Na were added to 1000 ml. of Developer-1.

Developer-5: 0.1 g. of ferric sulfate and 2 g. of NTA were added to 1000 ml. of Developer-1.

Developer-6: 0.1 g. of ferric sulfate and 2 g. of Compound 1 were added to 1000 ml. of Developer-1.

EDTA–2Na: disodium ethylenediaminetetraacetate.

NTA: nitrilotriacetic acid.

Developer-2 to Developer-6 were also adjusted to pH 10.6.

Then, the color photographic material was subjected to the processing, i.e., stop fixing—washing—bleaching—washing—hardener fixing—washing—stabilizing—drying. The stop-fixing bath contains ammonium thiosulfate, the bleaching bath contains potassium ferricyanide, the hardener fixing bath contains ammonium thiosulfate and formalin and the stabilizing bath contains sodium metaborate.

The following table shows the degree of staining when treated with Developer-1 to Developer-6. Since the stain formed by this treatment was brown, it was shown by the blue optical density on a non-exposed area.

Developer No.:	Blue optical density
1	0.11
2	0.32
3	0.21
4	0.22
5	0.20
6	0.11

As is evident from this table, the color developer containing ferric ion results in a large amount of staining, which can be inhibited completely by adding Compound 1.

When commercially available color films and color printing papers were treated also, similar results were obtained.

EXAMPLE 2

A color light-sensitive material having, on an acetate film support, a blue-sensitive silver iodobromide emulsion layer containing a yellow coupler, a gelatin intermediate layer, a red-sensitive silver chlorobromide emulsion layer containing a cyan coupler, a gelatin intermediate layer, a green-sensitive silver chlorobromide emulsion layer containing a magenta coupler and a gelatin protective layer was treated at 21° C. for 12 minutes with the developing solution described in Journal of the SMPTE 61, 12, 667 (1953) and with the same solution but to which the compounds of this invention were added.

Developer-7:	(pH 10.65) g.
Calgon (trade name) ----------	2.0
Sodium sulfite ----------	4.0
N,N-diethyl - p - phenylenediamine (hydrochloride) ----------	3.0
Sodium carbonate (monohydrate) ----------	20.0
Potassium bromide ----------	2.0
Water to 1000 ml.	

Developer-8: 2 g. of hydroxylamine (hydrochloride) was added to 1000 ml. of Developer-7.

Developer-9: 1 g. of Compound 1 was added to 1000 ml. of Developer-7.

Developer-10: 1 g. of Compound 4 was added to 1000 ml. of Developer-7.

Developer-11: 1 g. of Compound 5 was added to 1000 ml. of Developer-7.

Developer-12: 1 g. of Compound 6 was added to 1000 ml. of Developer-7.

Developer-8 to Developer-12 were also adjusted to pH of 10.65.

The treatment was carried out in the order of prebath — rinse — development — rinse — fixing — washing — leaching — washing — fixing — washing —stabilizing — drying. The prebath contained caustic soda and the bleaching bath contained potassium dichromate. The other baths were similar to those of Example 1.

The following table shows the degree of fog formed when treated with Developer-7 to Developer-12. This treatment was carried out using a tray. The aerial fog appearing in any of the cyan, magenta and yellow layers, particularly strong in the cyan layer, is represented by the red optical density on a non-exposed area.

Developer No.:	Red optical density
7	0.31
8	0.12
9	0.10
10	0.10
11	0.10
12	0.10

As is evident from this table, the color developer containing no antioxidant produced a market aerial fog. In using Developer-8, there was a considerable air for inhibiting effect but not so sufficient and the sensitivity was less than in using Developer-7. On the contrary, Developer-9 to Developer-12 containing the additives of the invention was substantially free from aerial fog, had no influence upon the photographic properties and was so stable that decomposition did not occur.

When commercially available color films and color printing papers were treated in the above manner, similar results were obtained.

EXAMPLE 3

A photographic printing paper having a silver chlorobromide emulsion layer on baryta paper was treated at 20° C. for 90 seconds with each of the following Developer-13 to Developer-16.

Developer-13:	G.
Metol (trade name) ----------	1.0
Sodium sulfite ----------	15.0
Hydroquinone ----------	4.0
Sodium carbonate (monohydrate) ----------	27.0
Potassium bromide ----------	0.7
Water to 1000 ml.	

Developer-14: 0.2 g. of ferric sulfate was added to 1000 ml. of Developer-13.

Developer-15: 0.2 g. of ferric sulfate and 0.5 g. of Compound 1 were added to 1000 ml. of Developer-13.

Developer-16: 0.2 g. of ferric sulfate and 0.5 g. of Compound 3 were added to 1000 ml. of Developer-13.

Then, the photographic material was subjected to fixing—washing—drying. The following table shows the degree of staining when treated with Developer-13 to Developer-16.

Since the stain formed by this treatment was brown, it was shown by the blue optical density on a non-exposed area.

Developer No.:	Blue optical density
13	0.03
14	0.10
15	0.03
16	0.04

As is evident from this table, the developer containing ferric ion results in a high degree of staining, which can be inhibited completely by adding Compound 1 or Compound 3.

When commercially available film and printing papers were treated in this manner, similar results were obtained.

What is claimed is:

1. A method of developing an exposed photographic light-sensitive silver halide material which comprises developing said material in a developer containing a compound selected from the group consisting of an inositolpolyphosphoric acid and an alkali metal salt thereof.

2. The method according to claim 1 wherein said compound contained in said developer is selected from the group consisting of a sodium salt of inositolpolyphosphoric acid and a potassium salt of inositolpolyphosphoric acid.

3. The method according to claim 1 wherein said compound contained in said developer is selected from the group consisting of inositolhexaphosphoric acid, inositolpentaphosphoric acid, inositoltetraphosphoric acid, 9Na inositolhexaphosphate, 11Na inositolhexaphosphate and 7K inositolhexaphosphate.

4. The method of developing an exposed color photographic light-sensitive silver halide material which comprises developing said material in a color developer containing a compound selected from the group consisting of an inositolpolyphosphoric acid and an alkali metal salt thereof.

5. The method of developing an exposed black and white light-sensitive silver halide material which comprises developing said material in a black and white developer containing a compound selected from the group consisting of an inositolphosphoric acid and an alkali metal salt thereof.

6. In a composition for developing a photographic light-sensitive silver halide material which comprises a developing agent and an alkali, the improvement which comprises said composition containing a compound selected from the group consisting of an inositolpolyphosphoric acid and an alkali salt thereof.

7. In a color developer composition for developing a color photographic light-sensitive silver halide material which comprises a color developing agent and an alkali, the improvement which comprises said composition containing a compound selected from the group consisting of an inositolpolyphosphoric acid and an alkali salt thereof.

References Cited

UNITED STATES PATENTS

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