United States Patent [19]

Brown

[11] **3,839,045**

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[54] **PHOTOGRAPHIC COLOR DEVELOPER SOLUTION STABILIZED WITH LITHIUM IONS**

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[22] Filed: **June 8, 1973**

[21] Appl. No.: **368,167**

Related U.S. Application Data

[62] Division of Ser. No. 224,627, Feb. 8, 1972, Pat. No. 3,794,591.

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

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

[58] **Field of Search** 96/66, 66.4

[56] **References Cited**

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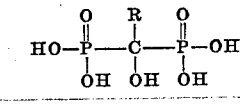
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Primary Examiner—Mary F. Kelley

Attorney, Agent, or Firm—A. P. Lorenzo

[57] **ABSTRACT**

The incorporation of small amounts of lithium ion into a solution of a heavy metal sequestering agent of the formula:



wherein R is a lower alkyl radical having from one to five carbon atoms, inhibits the formation of the white precipitate characteristically produced when sequestrants of this type are used to sequester ions of heavy metals such as calcium. Alkali metal, ammonium and ethanolamine salts of compounds of the above formula and mono and dialkyl esters thereof with methanol, ethanol, propanol and butanol also provide useful sequestering agents.

13 Claims, No Drawings

PHOTOGRAPHIC COLOR DEVELOPER SOLUTION STABILIZED WITH LITHIUM IONS

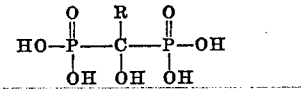
This is a division of application Ser. No. 224,627 filed Feb. 8, 1972, and issued Feb. 26, 1974, as U.S. Pat. No. 3,794,591.

FIELD OF THE INVENTION

The present invention relates to improved methods for sequestering heavy metal ions and in particular to photographic developer solutions which contain such heavy metal ion sequestering agents and small amounts of lithium.

BACKGROUND OF THE INVENTION

U.S. Pat. No. 3,214,454 to Blaser et al., issued Oct. 26, 1965 describes the preparation of organic acylation products of phosphorous acid and particularly compounds of the formula:



wherein R is a lower alkyl group having from one to five carbon atoms and the use of these materials as complex formers (sequestering agents) for metal ions and particularly polyvalent metal ions.

The utility of these compounds as sequestering agents and their exceptional abilities as complex formers of heavy metal ions is well known by those skilled in this art. However, these materials do have at least one relatively major shortcoming. This shortcoming is clearly manifested when compounds of the class described are used to sequester, for example, calcium from an alkaline solution which also contains, for example, sodium or potassium ion. In such a sytem a characteristic white precipitate, which is readily recognized by the skilled artisans in this field, forms after a very short period of time.

Im many usages, and in particular in photographic development, this precipitate can produce deleterious effects some of which are similar to those which prompted addition of the sequestrant initially.

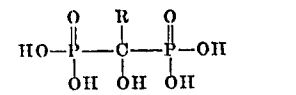
OBJECTS OF THE INVENTION

It is therefore an object of the present invention to provide a method of sequestering, for example, calcium ion from a solution using the aforementioned acylation products of phosphorous acid which method eliminates the formation of the characteristic white precipitate.

Yet another object of the present invention is the provision of sequestering solutions of the aforementioned organic acylation products of phosphorous acid (and in particular color photographic developer solutions) which when used to sequester, for example, calcium ion, do not produce the aforementioned white precipitate.

SUMMARY OF THE INVENTION

According to the present invention, the formation of a white precipitate when an organic acylation product of phosphorus acid and in particular compounds of the formula



wherein R is a lower alkyl group having from one to five carbon atoms, is used to sequester heavy metal ions, especially calcium, is inhibited by the addition of small amounts of lithium ion to the sequestering agent solution.

DETAILED DESCRIPTION OF THE INVENTION

In a solution containing alkali metal ions other than lithium, for example, sodium and potassium ions as well as polyvalent metal ions, attempts to sequester the polyvalent metal ions with organic acylation products of the type described above and in U.S. Pat. No. 3,214,454 have resulted in the formation of a white precipitate. It has now been discovered that the incorporation of at least about 100 ppm of lithium ion in such a solution inhibits the formation of such a white precipitate.

These acylation products can be produced, e.g., by reacting phosphorous acid with acid anhydrides and/or acid chlorides, especially those of acetic, propionic, butyric, valeric and caproic acid. When both the anhydride and the chloride are used simultaneously, they must be derived from the same acid, e.g., the anhydride and the chloride of acetic acid can be used simultaneously, but not acetic anhydride together with propionic chloride. In lieu of phosphorous acid and one of the acid chlorides named above, phosphorus trichloride can be reacted with one of the carboxylic acids themselves. Particularly readily available are the reaction products of phosphorous acid with acetic anhydride, with acetyl chloride or with a mixture thereof. The reactions opportunely are carried out at elevated temperatures, preferably between 50° and 200°C.

As described in the aforementioned U.S. Pat. No. 3,214,454 the concentration of sequestering agent may range from 1 mol per 5000 mols of metal up to stoichiometric quantities of sequestering agent and polyvalent metal ion.

According to a preferred embodiment of the present invention wherein the organic acylation product of phosphorous acid is used as a sequestering agent in a photographic developer the concentration of lithium ion ranges between about 100 and 450 ppm. Below this range insufficient lithium is present to inhibit precipitate formation while at concentrations substantially above this range undesirable sensitometric effects occur which make use of such levels of lithium in a photographic environment practically impossible.

In solutions of sequestering agents of the type described above, which solutions are used in an environment other than that of a photographic developer, the effective upper limit of lithium ion concentration can be governed by one or more of the following factors: (1) tolerance of the solution for lithium ion; (2) the upper limit of solubility of the source of lithium ion in the particular solution; and (3) perhaps in some cases toxicity levels of lithium compounds which might to some degree limit their use.

The lithium ion can be supplied to the solution of sequestering agent in any suitable form. This generally will be as a soluble salt of lithium, for example as lithium sulfate, lithium sulfite, lithium hydroxide, etc. In photographic developer compositions which have very

sensitive balances of a variety of ions for example, sulfite, sulfate, buffer (i.e. borate, carbonate, etc.) and halogen ion it is generally advisable to add the lithium as a salt whose anion is common to the system and compatible therewith. For example, when a carbonate buffer is used in such a system, the lithium is advantageously added as lithium carbonate. In a developer which contains a sequestering agent of the type described and a borate buffer the lithium is advantageously added as lithium hydroxide. Similarly lithium sulfate is preferred when the developer contains hydroxylamine sulfate. Since it is generally advisable to maintain a low halogen ion concentration in photographic developers, the addition of lithium as lithium chloride, bromide or iodide generally produces undesirable sensitometric effects, however, in other sequestering mediums where halogen ion content produces no adverse effect lithium ion can be provided in the form of a halogen salt.

Although the concentration of lithium in the sequestering bath may vary broadly within the limits described above, superior results are achieved when the ratio of lithium ion to other alkali metal ions in the solution ranges from about 0.5 to 1.5 : 1. At this level of lithium ion substantially complete freedom from undesirable precipitate is noted.

Similarly, although the improved results of the instant invention are achieved when almost any polyvalent metal ion is being sequestered (for example, Mg^{+2}, Ca^{+2}, Cu^{+2}, Zn^{+2} and Fe^{+3}) the most obvious improvement is obtained in solutions used to sequester calcium in (Ca^{+2}) since it is in this medium that the most aggravated precipitation occurs, particularly in the photographic field where sequestering agents of this type are used as anti-calcium agents.

Although applicant does not wish to be bound by any particular theory for the mechanism of his invention it is believed that in solutions containing polyvalent metal ions, (Ca^{+2}, Cu^{+2} etc.) a sequestering agent of the type described and alkali metal ions other than lithium, for example, sodium and/or potassium the dialkali, monopolyvalent ion salt of the sequestering agent is formed and it is this species which precipitates. Thus, where the solution contains sodium and calcium ion, the disodium, monocalcium salt of the sequestering agent would form the precipitate. In the case where both sodium and potassium were present in the solution the precipitate formed could be the disodium, dipotassium or monosodium, monopotassium, monocalcium salt of the sequestering agent, etc.

From this, or any other theory for the formation of the precipitate, it seems very surprising that the addition of further amounts of an alkali metal ion, namely lithium, would provide any beneficial effect let alone the elimination of the precipitate which presumably includes alkali metal ion.

The following examples will serve to demonstrate the invention described herein.

EXAMPLE 1

A photographic developer solution having the following composition

Hydroxylamine sulfate	4.5 gm
Sodium Hydroxide (50 %)	80 gm
Benzyl alcohol	15.7 ml
Potassium hydroxide	51 gm
sodium sulfite	1.9 gm
Boric acid	19.0 gm
4-amino-N-ethyl-N[β-methanesulfonamidoethyl]-m-toluidine (sequisulfate monohydrate)	5.3 gm
Sufficient water to make	1 liter

was prepared and utilized to develop imagewise exposed, silver coupler color print material. To this seasoned solution were added the amounts of calcium ion, and organic phosphorous acid sequestering agent, indicated in Table I below.

TABLE I

Ca++	60% aqueous solution of Sequestering Agent	Results after 38 days
350 ppm	2 ml/l	Precipitate
300 ppm	2 ml/l	Precipitate
250 ppm	2 ml/l	Precipitate
200 ppm	2 ml/l	Precipitate
150 ppm	2 ml/l	Precipitate

Thus, precipitate formed at all of these levels of Ca++ when the organic phosphorous acid derivative was used as sequestrant.

EXAMPLE 2

The method of Example 1 was repeated except that the addition to the seasoned developer comprised:

0.25 M K_2CO_3, 1 ml/l 60 percent aqueous solution of sequestering agent* and 100 ppm Ca++

In addition to the foregoing the additions shown in Table II were incorporated into the seasoned developer and the results indicated.

TABLE II

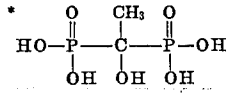
Additive	Result
Standard (no further additive)	Precipitate (3 days)
1 g/l potassium hexametaphosphate	Precipitate (3 days)
0.05 M Li+	No precipitate
0.05 M Rb+	Precipitate (3 days)
0.05 M Cs+	Precipitate (3 days)

EXAMPLE 3

An aqueous solution comprising 0.25 M K_2CO_3, 1 ml/l of a 60 percent aqueous solution of organic phosphorous acid sequestering agent* and 100 ppm of Ca++ was prepared. To this solution the additions indicated in Table III were made. The approximate weight of precipitate formed after 10 and 17 days is shown in Table III.

TABLE III

Additive	10 days	17 days
0.01 M Na_2CO_3	0.704	0.790
1 g/l potassium hexametophosphate	0.715	0.810
0.05 M. Li+	>0.001	0.006
0.05 M Rb+	~.700	0.844
0.05 M Cs+	~.700	Na

* 

From the foregoing examples, it should be clear that the incorporation of small amounts of Li+ with the organic phosphorous acid sequestering agent inhibits formation of the precipitate formed when this material is used as sequestering agent.

EXAMPLE 4

The following Table IV gives the time (in days) until noticeable precipitate formed in an aqueous 0.25 M K_2CO_3 solution containing 1 ml/l of a 60 percent aqueous solution of 1-hydroxyethylidene-1,1-diphosphonic acid.

TABLE IV

	Na^+ Concentration 0.2 M		0.1 M		0.04 M		0.02 M	
Ca^{++} Conc. (ppm)	100	200	100	200	100	200	100	200
Li^+ Conc.								
0.2 M	—	—	—	—	—	—	—	—
0.1 M	48 days	—	—	—	—	—	—	—
0.04 M	13 days	20 days	48 days	48 days	—	—	—	—
0.02 M	13 days	20 days	20 days	48 days	—	—	—	—
0.00 M	1 day		7 days		68 days	—	—	—

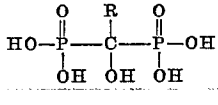
From the foregoing Example 4, it should be clear that highest stability (ie., resistance to precipitation) for solutions containing calcium is achieved when the weight ratio of lithium ion to other alkali metal ions is at least about 0.02:1. Further improved results are achieved when this ratio is at least about 0.05:1 and optimum results are achieved at the level where this ratio is at least about 0.1:1. The upper limit of this ratio will depend to a large extent upon the concentration and solution tolerance factors described above. Thus, no absolute upper limit can be described, however, as a practical matter, lithium to other alkali metal ion ratios above about 10:1 would appear to serve no useful purpose particularly in photographic developer compositions.

The invention has been described in detail with particular reference to the preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. An aqueous alkaline photographic color developer solution comprising

1. a color developing agent,
2. polyvalent metal ions,
3. a sequestering agent for said polyvalent metal ions, said sequestering agent being selected from the group consisting of
   a. phosphorus compounds of the formula



where R is an alkyl group of from one to five carbon atoms,

   b. alkali metal, ammonium and ethanolamine salts of said phosphorus compounds, and
   c. monoalkyl and dialkyl esters of said phosphorus compounds with methanol, ethanol, propanol or butanol,
4. alkali metal ions selected from the group consisting of sodium ions and potassium ions in a concentration capable of resulting in the formation of a precipitate of said sequestering agent, and
5. lithium ions in a concentration sufficient to substantially prevent formation in said solution of a precipitate of said sequestering agent.

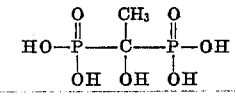
2. A solution as claimed in claim **1** wherein said sequestering agent is present in said solution in an amount of from about 1 mole per 5000 moles of polyvalent metal ion up to stoichiometric quantities based on the total polyvalent metal ion concentration and the concentration of lithium ions in said solution is at least about 100 ppm.

3. A solution as claimed in claim **1** wherein said polyvalent metal ions are calcium ions.

4. A solution as claimed in claim **1** wherein said alkali metal ions are sodium ions.

5. A solution as claimed in claim **1** wherein said alkali metal ions are potassium ions.

6. A solution as claimed in claim **1** wherein said sequestering agent is the compound of the formula:



7. A solution as claimed in claim **1** wherein the concentration of said lithium ions is from about 100 ppm to about 450 ppm.

8. A solution as claimed in claim **1** wherein the weight ratio of said lithium ions to said alkali metal ions is at least about 0.02 to 1.

9. A solution as claimed in claim **1** wherein the weight ratio of said lithium ions to said alkali metal ions is at least about 0.05 to 1.

10. A solution as claimed in claim **1** wherein the weight ratio of said lithium ions to said alkali metal ions is in the range from about 0.5:1 to about 1.5:1.

11. A solution as claimed in claim **1** additionally containing hydroxylamine sulfate, sulfite ion and benzyl alcohol.

12. A solution as claimed in claim **1** wherein said color developing agent is 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate.

13. An aqueous alkaline photographic color developer solution comprising

1. a color developing agent,
2. calcium ions,
3. a sufficient amount of 1-hydroxyethylidene-1,1-diphosphonic acid to sequester said calcium ions,
4. sodium or potassium ions in an amount capable of resulting in the formation of a precipitate of the 1-hydroxyethylidene-1, 1-diphosphonic acid, and
5. lithium ions in an amount sufficient to substantially prevent the formation of a precipitate of the 1-hydroxyethylidene-1, 1-diphosphonic acid.

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