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PHOTOGRAPHIC SILVER HALIDE DEVELOPING SOLUTIONS CONTAINING CALCIUM PRECIPITATION INHIBITORS

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This invention relates to photography and particularly to methods and materials for preventing precipitation of calcium or other insoluble salts in photographic developers and other solutions.

The precipitation of insoluble calcium salts in water is a problem in many industries and is particularly objectionable in the photographic industry because of its effect on the quality of photographic films and the usability of photographic processing solutions. The use of certain complex phosphates, especially polymerized sodium metaphosphate and sodium or potassium pyrophosphates, in photographic developers to reduce the formation of calcium sulfite scum on the films and calcium precipitates in the developer is known. Upon standing in aqueous solutions, all of these phosphates gradually hydrolyze to the orthophosphates (Na_3PO_4, Na_2HPO_4 or NaH_2PO_4, depending upon the pH) which not only possess no inhibiting properties but may also precipitate the calcium themselves as the flocculent calcium orthophosphates. In addition to this difficulty, the addition of an excess of these inhibitors to alum fixing baths as when carried over from the developer, causes the precipitation of aluminum phosphate.

If the metaphosphate and pyrophosphate are expressed in terms of the ratio of sodium oxide to phosphorus pentoxide, it will be seen that sodium metaphosphate has the formula $Na_2O \cdot P_2O_5$, and sodium pyrophosphate has the formula $2Na_2O \cdot P_2O_5$.

In the copending application, Serial No. 751,122, filed May 28, 1947, now U. S. Patent 2,541,470, granted February 13, 1951, of which I am a joint inventor, is disclosed the effect of various polyhydroxycarboxylic acids on calcium precipitation in aqueous solutions.

I have discovered that if diglycolic acid and its alkali metal salts are used alone or in conjunction with a phosphate of the type indicated hereinafter, it is very much more effective in the prevention of calcium precipitation and the precipitation of other insoluble salts than are the polyhydroxy carboxylic acids, or any other acids previously used for this purpose. Moreover, in certain instances in photographic developers, the acid exerts a preservative effect.

It is, therefore, an object of the present invention to provide a method for preventing precipitation of insoluble calcium salts in water. A further object is to provide a method for preventing the precipitation of calcium and the formation of a calcium sulfite scum on photographic films when treated in a developing bath. Other objects will appear from the following description of my invention.

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These objects are accomplished by using either diglycolic acid alone or in conjunction with alkali metal phosphates particularly as a calcium precipitation inhibitor. My invention includes aqueous systems, especially developer compositions, containing such compounds both in wet and dry form.

The phosphates particularly useful in my invention, in conjunction with diglycolic acid, for their sequestering properties, are the water-soluble "polyphosphates" also known as "molecularly dehydrated phosphates" having less water in proportion to P_2O_5 than orthophosphoric acid. (Schwartz and Munter, Ind. & Eng. Chem., 34, 32: 1942) and (Partridge Chem. & Eng. News, 27, 214:1949.) Accordingly, by the term "polyphosphate" I mean the water-soluble phosphates of the general formula $xM_2O \cdot yP_2O_5$, where M_2O represents an alkali metal oxide such as sodium, potassium or ammonium oxide, and the ratio of x to y is from 1 to 2. Included in this group are the following phosphates:

Sodium tripolyphosphate (5:3)
Sodium pyrophosphate (2:1)
Sodium tetraphosphate (3:2)
Sodium metaphosphate (1:1)
Sodium hexametaphosphate (1:1) glass
Sodium pentapolyphosphate (6:5)

While the phosphates contemplated as a part of my invention have the property of forming soluble complexes with metal salts such as calcium and magnesium salts to a limited extent, the addition of diglycolic acid and its soluble salts to aqueous systems materially delays the precipitation of insoluble salts and the effect obtained is greater than expected from the behavior of either the phosphate or diglycolic acid used alone, as will be seen from consideration of the data to be subsequently presented. The addition of diglycolic acid to aqueous developing compositions produces the same effect and delays the formation of calcium sludge normally formed when calcium salts are added as an impurity in the water or from the film in processing operations. Presumably, diglycolic acid forms soluble complexes with the calcium salts, as do other organic acids such as those mentioned in the above copending application. However, the calcium complex of diglycolic acid appears to be more stable than the calcium complexes of the other acids and of the phosphates since a developer composition containing diglycolic acid can be held at the boiling point for from six to seven hours without loss of its sequestering power.

Sodium hexametaphosphate and sodium pyrophosphate and various organic acids have pre-

viously been used in photographic developer compositions, and sodium tetraphosphate is disclosed in the mentioned copending invention for the same purpose together with various polyhydroxy acids. Similarly, diglycolic acid and its salts are useful with improved results as can be seen by consideration of the following comparative tests.

Acids such as ethylenediamine tetraacetic acid and triglycin materially accelerate the rate of oxidation of developer solutions particularly in the presence of minute quantities of iron. For example, a developer containing 0.5 per cent of triglycin together with eight parts per million of iron and two parts per million of copper caused very rapid oxidation of the developer when air was bubbled through the solution for two hours. When the developer was formulated with diglycolic acid instead of triglycin, the developer withstood similar aeration for 30 hours.

When sodium tetraphosphate was used alone as a sequestering agent in a developer composition of the type set forth in detail hereinafter at pH of 10, it lost 70 per cent of its activity after one hour at 95° C. When diglycolic acid was used in formulating the developer instead of the phopshate, no loss of activity was noted after six hours at 95° C.

These data constitute positive evidence of the improved effectiveness of diglycolic acid as a stabilizing agent for the prevention of calcium precipitation on storage of developer compositions. Diglycolic acid is a stronger sequestering agent than acids such as citric, gluconic and tartaric acids. For example, 50 grams of diglycolic acid incorporated into a liter of developer sequestered nine grams of calcium chloride under the conditions of test. At equal concentrations, soduim citrate sequestered two grams; sodium gluconate, 1.5 grams; and sodium potassium tartrate, 1.5 grams of calcium chloride. Similarly, glycolic acid had no effect as a sequestering agent at a concentration at which diglycolic was highly effective.

Diglycolic acid is more effective in the prevention of calcium precipitation in silver halide developers containing borate salts, than in developers containing carbonate as the alkaline material; however, very useful results are obtained in either case. Typical developers to which diglycolic acid can be added alone or in conjunction with the phosphates indicated above are the following:

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Monomethyl-p-aminophenol sulfate	g	2
Hydroquinone	g	5
Sodium sulfite desiccated	g	100
Borax	g	2
Water to liter		1

II

Monomethyl-p-aminophenol sulfate	g	3.1
Hydroquinone	g	12
Sodium sulfite, desiccated	g	45
Sodium carbonate, desiccated	g	67.5
Potassium bromide	g	1.9
Water to liter		1

In addition to protecting the developer against calcium precipitation, the employment of the acid of my invention particularly in conjunction with phosphate, will greatly reduce the tendency for aluminum phosphate to be formed in the fixing bath and will reduce the attendant sludge.

The use of these inhibitors need not be confined to the developer but may be extended to other baths where an insoluble calcium precipitate, aluminum precipitate or precipitate of other polyvalent metal occurs. For example, certain wetting agents used for drying film precipitate with hard water or with aluminum contaminant from the fixing bath. Small quantities of a combination of phosphate and the acid effectively inhibit this precipitation.

The results obtained by using diglycolic acid in a developer are shown by a consideration of the following formulas of representative developers in which the quantities given are expressed in terms of grams per liter of solution.

	III	IV
	grams	*grams*
Monomethyl-p-aminophenol sulfate	2.5	2.5
Hydroquinone	2.5	2.5
Sodium sulfite (anhydrous)	50.0	50.0
Sodium metaborate	20.0	20.0
Diglycolic acid		50.0
Sodium hydroxide, 95%		30.0

Developer III was found to precipitate insoluble salt with the addition of 0.15 gram of calcium chloride per liter, while developer IV permitted the addition of 8 grams of calcium chloride per liter without precipitation even after heating and allowing the developer to stand.

The improved results obtained with a carbonate-containing developer are shown by diluting developer II above (one part of developer to two of water) and then adding 50 grams of diglycolic acid and sufficient sodium hydroxide to neutralize the acid. As compounded, the developer was protected against addition of 1.5 grams of calcium chloride per liter, whereas without the addition of glycolic acid, insoluble salt was precipitated in the same developer by the addition of less than 0.1 gram of calcium chloride per liter.

In addition to the mentioned instability of phosphate complexes, it is difficult to prevent the precipitation of the large quantities of calcium introduced into a developer by the film when employing the polyphosphates alone, even in high concentrations. In developers employing metaborate as the alkaline material, optimum sequestering obtainable with polyphosphates still results in the formation of considerable calcium sludge. This sludge is almost completely prevented by the addition of diglycolic acid to supplement the action of the phosphate. In practice, the acid is generally added to the replenisher solution to compensate for the calcium salt being continuously introduced as the film passes into the developer. Comparison of the following developer formulas and consideration of the amount of sludge obtained show the effect of the use of diglycolic acid. In the formulas, the ingredients are expressed in terms of grams per liter of solution and of course diglycolic acid can be used in developer V as well as in the replenisher formulas.

	Developer V	Replenisher A	Replenisher B
	Grams	*Grams*	*Grams*
Monomethyl-p-aminophenol sulfate	2.5	5.0	5.0
Hydroquinone	2.5	10.0	10.0
Sodium sulfite	60.0	60.0	60.0
Sodium metaborate	10.0	40.0	40.0
Sodium hydroxide		4.0	8.5
Sodium tetraphosphate	0.5	1.0	1.0
Diglycolic acid			7.5

A further characteristic of diglycolic acid when used for the prevention of the precipitation of

insoluble salts in water is its effectiveness over a wide range of pH. For example, sodium hydroxide was added to several one per cent solutions of diglycolic acid to adjust the pH over the range of 2 to 12. Sodium fluoride was added as an indicator, and then as varying quantities of calcium chloride were added, the mixtures were allowed to stand. In the absence of the diglycolic acid, precipitates were formed with very low concentrations of calcium chloride. Over the pH range of 4 through 10, 0.5 gram of diglycolic acid successfully sequestered 0.1 gram of calcium chloride. The sequestering action decreased somewhat at pH values of 2 and 12. A similar but more pronounced effect is obtained if a polyphosphate is also present. Accordingly, the use of diglycolic acid as a sequestering agent is not limited to alkaline developer compositions but can be used in acid systems as well, for example, acid photographic fixing baths. Similarly, it has been found that the addition of as little as 0.1 per cent of neutral diglycolic acid to ordinary tap water will largely prevent the formation of scale usually obtained in heating water, for example, in boiler tubes.

The following examples further illustrate my invention.

EXAMPLE 1

The following compositions are packaged ready for dissolving in one liter of water to make a photographic developing solution:

Compartment A

	Grams
Monomethyl-p-aminophenol sulfate	5
Hydroquinone	2.5

Compartment B

	Grams
Sodium sulfite (anhydrous)	60
Sodium metaborate	20
Diglycolic acid	50
Sodium hydroxide	30

EXAMPLE 2

Compartment A

	Grams
Monomethyl-p-aminophenol sulfate	10
Hydroquinone	5
Sodium tetraphosphate	1

Compartment B

	Grams
Sodium sulfite	60
Sodium metaborate	40
Sodium hydroxide	8.5
Diglycolic acid	7.5

The chemicals are then added to one liter of water.

EXAMPLE 3

If desired, in Example 2, the diglycolic acid can be placed in Compartment A rather than in Compartment B.

EXAMPLE 4

In any of the above solid mixtures containing alkali-metal polyphosphates, the tendency of the polyphosphate to fuse or become tacky on exposure to moist air may be overcome by mixing an inert alkali-metal sulfate, such as anhydrous sodium or potassium sulfate, with the polyphosphate. A mixture of one part of sodium tetraphosphate with two parts of anhydrous sodium sulfate or potassium sulfate was found to remain free flowing upon an exposure to an atmosphere of 70 per cent relative humidity for two weeks. The concentration may vary from one part of polyphosphate in from ½ to 20 parts of alkali-metal sulfate.

EXAMPLE 5

The presence of iron in some polyphosphates may cause increased development fog. This fog may be controlled by the addition of antifoggants such as alkali-metal bromides and iodides, or organic antifoggants such as 1,2,3-benzotriazole and 6-nitrobenzimidazole. A sample of sodium hexametaphosphate containing 0.03 per cent of iron was found to give bad fog when added to developing solutions for high speed negative emulsions. The presence of 0.05 gram of 1,2,3-benzotriazole per gram of sodium hexametaphosphate prevented this fog.

The concentration of antifoggant may vary from 1 part of antifoggant to from 2 to 100 parts of phosphate in the case of potassium iodide, 1,2,3-benzotriazole and 6-nitrobenzimidazole nitrate and from 1 part of antifoggant to from 0.1 to 10 parts of phosphate in the case of potassium bromide.

In photographic developing solution useful results are obtained by using from about 2 to 100 grams per liter of solution of diglycolic acid or its alkali metal salts, particularly in conjunction with from about .05 to 20 grams per liter of polyphosphate. These ranges are particularly useful in conjunction with alkali metal tetraphosphates and hexametaphosphates.

The other polyphosphates indicated above besides sodium tetraphosphate can be added to any of the above formulas in dry or liquid form.

Diglycolic acid can be added to the hydrazine-containing developer compositions disclosed in the Ives application, Serial No. 192,380, filed October 26, 1950, now U. S. Patent No. 2,588,982, granted March 11, 1952, and the Bean et al. application, Serial No. 218,072, filed concurrently herewith, which are used in making direct positive images. In this case, diglycolic acid is employed especially as a preservative as well as functioning as a sequestering agent.

I claim:

1. An alkaline photographic developing solution comprising a silver halide developer and a compound selected from the class consisting of diglycolic acid and its alkali metal salts.

2. An alkaline photographic developing solution comprising a silver halide developer, a water-soluble alkali metal polyphosphate and a compound selected from the class consisting of diglycolic acid and its alkali metal salts.

3. An alkaline photographic developing solution comprising a silver halide developer, a water-soluble alkali metal polyphosphate having the formula $xM_2O \cdot yP_2O_5$ where M is an alkali metal, and x and y represent numbers in which the ratio of x to y is from 1 to 2, an alkaline material, and a compound selected from the class consisting of diglycolic acid and its alkali metal salts.

4. An alkaline photographic developing solution comprising a silver halide developer, a water-soluble metal salt of tetraphosphoric acid, an alkaline material, and a compound selected from the class consisting of diglycolic acid and its alkali metal salts.

5. An alkaline photographic developing solution comprising a silver halide developer, from .05 to 20 grams per liter of a water-soluble alkali metal polyphosphate, an alkaline material, and from 2 to 100 grams per liter of a compound selected from the class consisting of diglycolic acid and its alkali metal salts.

6. An alkaline photographic developing solution comprising a silver halide developer, from .05 to 20 grams per liter of a water-soluble alkali metal salt of tetraphosphoric acid, and from 2 to 100 grams per liter of a compound selected from the group consisting of diglycolic acid and its alkali metal salts.

7. An alkaline photographic developing solution comprising a silver halide developer, from .05 to 20 grams per liter of a water-soluble alkali metal hexametaphosphate, and from 2 to 100 grams per liter of a compound selected from the class consisting of diglycolic acid and its alkali metal salts.

8. A photographic developer in dry form comprising a silver halide developer, an alkaline material and a compound selected from the group consisting of diglycolic acid and its alkali metal salts.

9. A photographic developer in dry form comprising a silver halide developer, an alkaline material, a compound selected from the group consisting of diglycolic acid and its alkali metal salts, and a water-soluble alkali metal polyphosphate.

10. A photographic developer in dry form comprising a silver halide developer, sufficient water-soluble alkali metal polyphosphate having the formula $xM_2O \cdot yP_2O_5$ where M is an alkali metal, and x and y represent numbers in which the ratio of x to y is from 1 to 2, to produce .05 to 20 grams per liter in solution, a sufficient amount of a compound selected from the class consisting of diglycolic acid and its alkali metal salts to produce 2 to 200 grams per liter in solution, and sufficient alkaline material to produce an alkaline developer solution when the mixture is dissolved in water.

11. A photographic developer in dry form comprising a silver halide developer, sufficient water-soluble alkali metal salt of tetraphosphoric acid to produce .05 to 20 grams per liter in solution, a sufficient amount of a compound selected from the class consisting of diglycolic acid and its alkali metal salts to produce 2 to 200 grams per liter in solution, and sufficient alkaline material to produce an alkaline developer solution when the mixture is dissolved in water.

12. A photographic developer in dry form comprising a silver halide developer, sufficient water-soluble alkali metal hexametaphosphate to produce .05 to 20 grams per liter in solution, a sufficient amount of a compound selected from the class consisting of diglycolic acid and its alkali metal salts to produce 2 to 200 grams per liter in solution, and sufficient alkaline material to produce an alkaline developer solution when the mixture is dissolved in water.

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No references cited.