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# PHOTOGRAPHIC DEVELOPERS CONTAINING CALCIUM PRECIPITATION INHIBITORS

Charles F. H. Allen, John A. Ford, and Richard W. Henn,  
Rochester, N.Y., assignors to Eastman Kodak Com-  
pany, Rochester, N.Y., a corporation of New Jersey  
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This invention relates to photographic developing compositions containing amino-N,N-dimethylenephosphonic acids and their water-soluble derivatives.

Most silver halide photographic developing solutions contain anions, such as carbonate, sulfite, or borate, which form very sparingly soluble alkaline earth salts. Calcium, for example, may enter the developing solution from the photographic emulsion, particularly if gelatin is used as the silver halide peptizer, or calcium and magnesium may be present in the water used to prepare the developing solution. The resulting precipitates of, for example, calcium and magnesium carbonates, sulfites, and borates, form sludge or scum on the photographic materials and scale on the equipment, and, therefore, may have an adverse effect on the quality of the photographic film being processed.

Previously, the difficulty arising from the presence of calcium in developing compositions has been overcome to some degree by the use of compounds which complex with calcium in the un-ionized form. For example, alkali hexametaphosphates and polyphosphates, e.g., alkali tetraphosphates, have been used in developing solutions to reduce the formation of the calcium sulfite scum on the films, and precipitation of calcium in the developer. However, when these phosphates stand in aqueous solutions, they gradually hydrolyze to the orthophosphates which do not inhibit calcium precipitation and may precipitate the calcium in the form of calcium phosphate. Also, if orthophosphate is carried over to an alum fixing bath, there is the possibility of the precipitation of aluminum phosphate.

Some oxygen acids, such as citric, tartaric, gluconic, diglycolic, etc., have proved to have some usefulness as calcium sequestering agents in photographic developing solutions, but the sequestering potency of these acids is comparatively weak and it may be necessary to supplement their effect, e.g., by adding polyphosphates, such as sodium tetraphosphate.

The use of certain aminopolyacetic acids as stable and effective sequestrants in developing solutions has also been previously disclosed. Some of these, such as ethylenediamine-tetracetic acid and nitrilotriacetic acid show a very considerable tendency to catalyze oxidation of the developer by the air in the presence of traces of iron. For example, a developer containing 0.5 percent of one of these materials, together with 8 p.p.m. of iron and 2 p.p.m. of copper, will cause very rapid oxidation of the developer when air is bubbled through the solution for 2 hours. They also tend to fog some photographic emulsions, particularly the high speed negative bromide types.

One object of our invention is to produce photographic developers having improved properties. Another object of our invention is to provide developer compositions which contain a calcium sequestering agent having good stability, high sequestering potency, low fogging propensity, and having little or no tendency to promote developer oxidation even though traces of iron and other materials may be present.

A further object of our invention is to prevent the formation of calcium-containing sludges, scums, and scales in the developer solutions. The use of our sequestering

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agents is not limited to the developer; they may also be employed in other processing baths where calcium precipitates are a problem, including prebaths, toners, bleaches, activators, washing accelerators etc. Other objects of our invention will appear herein.

The amino-N,N-dimethylenephosphonic acids and their water-soluble derivatives which can advantageously be employed in our invention include those represented by the following general formula:



wherein M represents a hydrogen atom or a cation which imparts water solubility, such as an alkali metal atom (e.g., sodium, potassium, etc.), ammonium, pyridinium, triethanol ammonium, triethyl ammonium etc., and R represents an alkyl group, such as methyl, ethyl, propyl, isopropyl, butyl, etc. (e.g., an alkyl group containing from 1 to 4 carbon atoms), an aryl group, such as phenyl, o-, m- and p-tolyl, o- and p-carboxyphenyl (and water-soluble salts thereof, such as sodium, potassium, etc.), an aralkyl group, such as benzyl  $\beta$ -phenethyl, o-acetamidobenzyl, etc. (e.g., an aralkyl group containing from 7 to 9 carbon atoms), an alicyclic group, such as cyclohexyl, cyclopentyl, etc. (e.g., an alicyclic group containing from 5 to 6 carbon atoms), or a heterocyclic radical, such as a heterocyclalkyl group (e.g., pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, etc.). The R group of Formula I above can be further substituted (especially where R represents an alkyl group) with a radical, such as hydroxyl,  $-PO_3M_2$ ,  $-CH_2PO_3M_2$ , or  $-N(CH_2PO_3M_2)_2$ , where M has the values given above, chlorine, alkoxyl (e.g., methoxyl, ethoxyl, etc.), etc.

As indicated above, the amino-N,N-dimethylenephosphonic acids used in our invention can be used in the form of the free acid, or they can be employed in the form of water-soluble salts. Of course, when the free acid is added to a strongly alkaline photographic developing solution of the type normally employed in photography, a water-soluble salt of the acid inherently forms. The sequestering agents of our invention can be prepared according to the procedures of Bersworth U.S. Patent 2,599,807, issued June 10, 1952. This method comprises reacting a chloromethylenephosphonic acid with an organic amine. Alternatively, these sequestering agents can be prepared as described by Westerback and Martell in Nature, vol. 178, page 321 (1956). Typical water-soluble sequestering agents which can be employed in our invention include the following:



ethylenediamine - N,N,N',N' - tetramethylenephosphonic acid (EDTMP). (Prepared from ethylenediamine and chloromethylenephosphonic acid.)



nitrilo - N,N,N-trimethylenephosphonic acid. (Prepared from ammonia and chloromethylenephosphonic acid.)

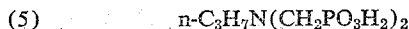


1,2 - cyclohexanediamine-N,N,N',N'-tetramethylenephosphonic acid. (Prepared from 1,2-diaminocyclohexane and chloromethylenephosphonic acid.)



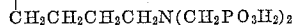
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o - Carboxyanilino - N,N - dimethylenephosphonic acid. (Prepared from anthranilic acid and chloromethylenephosphonic acid.)



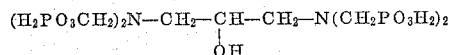
Propylamino - N,N - dimethylenephosphonic acid. (Prepared from n-propylamine and chloromethylenephosphonic acid.)

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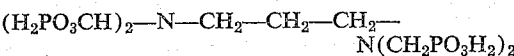
4 - (N-pyrrolidino)butylamine - N,N-bis(methylenephosphonic acid). (This can be prepared from 4-(N-pyrrolidino)butylamine and chloromethylenephosphonic acid.)

(7)



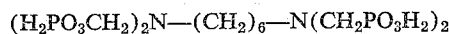
1,3 - diaminopropanol - N,N,N',N' - tetramethylenephosphonic acid (DPTP). (Prepared from 1,3-diaminopropanol and chloromethylenephosphonic acid.)

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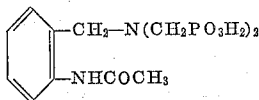
1,3 - propanediamine - N,N,N',N' - tetramethylenephosphonic acid. (Prepared from 1,3-propanediamine and chloromethylenephosphonic acid.)

(9)



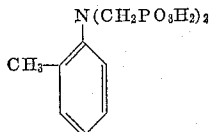
1,6 - hexanediamine-N,N,N',N'-tetramethylenephosphonic acid. (Prepared from 1,6-hexanediamine and chloromethylenephosphonic acid.)

(10)



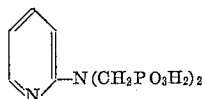
o - Acetamidobenzylamino - N,N-dimethylenephosphonic acid. (Prepared from o-acetamidobenzylamine and chloromethylenephosphonic acid.)

(11)



o-Toluidine - N,N - dimethylenephosphonic acid. (Prepared from o-toluidine and chloromethylenephosphonic acid.)

(12)



2 - pyridylamino - N',N' - dimethylenephosphonic acid. (Prepared from 2-aminopyridine and chloromethylenephosphonic acid.)

The phosphonic sequestering agents of our invention can be employed in photographic developing solutions of the type normally employed in black-and-white photography, or in color photography. They can also be employed in other photographic solutions where it is desired to remove unexposed silver halide, such as fixing or stabilizing solutions, or they can be added to wash baths or toning baths.

Typical black-and-white developing agents, which produce a negative silver image, include the polyhydroxy benzenes, such as hydroquinone, chlorohydroquinone, 2,5 - (dihydroxyethylamino)-hydroquinone, methylhydroquinone, etc., monoalkylaminophenols, such as N-methyl-p-aminophenol (sulfate or hydrochloride), etc., 3-pyrazolidones, such as 1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone, 4,4-diethyl - 1 - phenyl-3-pyrazolidone, etc.

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The color-forming developers useful in our invention have been previously described in the prior art and our invention is not restricted to the use of any particular color-forming developer. Particularly useful color-forming developers are the phenylenediamines and substituted derivatives thereof. Typical of such color-forming developers are the sulfonamido- substituted p-phenylenediamines disclosed in Weissberger et al. U.S. Patent 2,548,574, issued April 10, 1951, the substituted p-phenylenediamines disclosed in Weissberger et al. U.S. Patents 2,552,240-2, issued May 8, 1951, and the substituted p-phenylenediamines disclosed in Weissberger et al. U.S. Patent 2,566,271, issued August 28, 1951. Other phenylenediamine color-forming developing agents can be employed to like advantage in the developing solutions of our invention.

In addition to the usual alkaline agents, such as carbonate, alkali, etc., used in photographic developing solutions, other ingredients, such as antifoggants, e.g., benzotriazole, 6-nitrobenzotriazole, etc., development restrainers, e.g., potassium bromide, sodium iodide, etc., preservatives, such as alkali metal sulfites, e.g., sodium sulfite, etc., can be present. In color developers, other ingredients can be present, such as couplers for forming the color image by coupling with the oxidation products of the color developer.

The concentration of the sequestering agents of our invention can be varied widely in photographic developing solutions, depending upon the molecular weight of the particular sequestering agent, concentration of undesired calcium ions, etc. In general, we have found that from about 0.1 to 50 grams per liter of solution of the amino-N,N-dimethylenephosphonic acid or its derivative is quite satisfactory. A particularly useful range is from about 0.5 to 10 grams per liter of solution.

The following examples are intended only to illustrate and do not limit the invention.

#### EXAMPLE 1.—CALCIUM SEQUESTERING ABILITY

The effectiveness of ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid (EDTMP) as a sequestering agent against carbonate ion was determined by employing a 2.5 percent solution of sodium sesquicarbonate,



which buffers in the pH region of 10.0, common to photographic developers. The solution without addend was used as a control, the tetrasodium salt of ethylenediaminetetracetic acid (EDTA) was added to a second portion, and the heptasodium salt of EDTMP (Compound 1) was added to the third portion. This material was 66 percent pure, the diluent comprising sodium chloride. A 1 percent calcium chloride solution was added to this until a permanent precipitate was produced. The following values were established:

Addend	Concentration		CaCl <sub>2</sub> to Produce Ppt.	
	Grams per Liter	Mols per Liter	Mg. per Liter	Mols per Mol
Control (no addend).....	-----	-----	50	-----
EDTA · 2H <sub>2</sub> O (tetrasodium salt).....	5	0.012	1,400	1.02
EDTMP (heptasodium salt).....	10	0.0127	1,100	0.80

This represents a severe test since calcium carbonate is the least soluble calcium compound encountered in ordinary photographic practice.

#### EXAMPLE 2.—DEVELOPER OXIDATION

The addition of iron to a photographic developer will somewhat reduce its aeration life, for example, by 10 to 30 percent. However, the further addition of an amino-carboxylic acid complexing agent, such as ethylenedi-

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aminetetracetic acid (EDTA), will cause rapid oxidation, reducing the life to perhaps 10 to 20 percent normal. But with the phosphonic acid complexing agent, EDTMP, the life is actually increased to approach that of the iron-free developer.

The data in this run apply to the Kodak Developer D-76 to which was added 1 part of iron (as ferric chloride) per 100,000 parts of developer. The developer was then divided and sequestering agents added to parts 2 and 3. Small air bubbles were introduced into the developer through a sintered glass bubbler. As indicated in the following table, the developer containing the EDTA sequestering agent discolored about 10X as rapidly as the control while the developer containing the EDTMP lasted perhaps a third longer than the control. Tests for photographic activity confirmed the visual results.

Data for Kodak Developer D-76+iron

Addend	Condition After Bubbling Air For—				
	0 Hours	3 Hours	5 Hours	42 Hours	58 Hours
None:					
Hue.....	Cloudy..	Cloudy..	Cloudy..	Med. Brown	Very dark.
Activity <sup>1</sup> .....	0.96.....	.....	.....	1.10.....	0.10.....
EDTA:					
Hue.....	Clear.....	Med. Brown	Very dark	.....	.....
Activity <sup>1</sup> .....	0.92.....	0.78.....	0.00.....	.....	.....
EDTMP:					
Hue.....	Clear.....	Clear.....	Clear.....	Clear.....	Med. Brown
Activity.....	0.95.....	.....	.....	1.10.....	0.94.....

<sup>1</sup> Photographic Activity—density of a negative speed bromiodide emulsion, developed 10 min. at 68° F.

The composition of Kodak Developer D-76 is as follows:

Monomethyl-p-aminophenol sulfate	grams	2.0
Sodium sulfite, desiccated	do	100.0
Hydroquinone	do	5.0
Sodium tetraborate·10H <sub>2</sub> O	do	2.0
Water to make	liter	1.0

#### EXAMPLE 3

The photographic activity of the developer was not impaired by the addition of EDTMP sequestering agent. This is shown in the table below in which Kodak D-76 developer is compared with the same developer modified by the addition of 2 g. of the EDTMP, heptasodium salt, per liter. A negative speed bromiodide emulsion was exposed to a step wedge and developed in the two developers for 15 minutes at 68° F. Substantially equal values of speed, fog, and contrast were obtained.

	Gamma	Speed (Relative log E)	Gross Fog
Kodak Developer D-76.....	1.22	4.63	0.13
Kodak Developer D-76+EDTMP.....	1.21	4.67	0.12

#### EXAMPLE 4

One of the disadvantages of EDTA as a sequestering agent is a propensity to cause an increase in developer fog, particularly with very high speed films. The following data apply to a negative speed bromiodide emulsion, for example, developed for 10 minutes at 68° F., in Kodak Developer DK-50. It will be seen that while the addition of the EDTA caused bad fog, the addition of EDTMP caused no increase in fog.

Sequestering agent:	Net fog
None	0.16
EDTA, 10 grams per liter	0.73
EDTMP, 10 grams per liter	0.15

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The composition of Kodak Developer DK-50 is as follows:

Monomethyl-p-aminophenol sulfate	grams	2.5
Sodium sulfite, desiccated	do	30.0
Hydroquinone	do	2.5
Sodium metaborate·8H <sub>2</sub> O	do	10.0
Potassium bromide	do	0.5
Water to make	liter	1.0

#### EXAMPLE 5.—1,3-DIAMINOPROPANOL-TETRAMETHYLENEPHOSPHONIC ACID (DPTP)

This material was prepared by reacting 1,3-diaminopropanol with chloromethylenephosphonic acid. The reaction product contained about 50 percent by weight of the octasodium salt of the sequestrant and about 50 percent of the sodium chloride. It proved to be an effective sequestering agent when employed under the conditions of Example 1, sequestering 100 mg. of calcium chloride per gram, or 1.0 mole per mole of the DPTP. Used under the conditions of Example 2, it was found free from propensity to promote developer oxidation.

#### EXAMPLE 6.—1,3-PROPANEDIAMINE-N,N',N',N'-TETRAMETHYLENEPHOSPHONIC ACID

This compound was prepared by the methods described previously and obtained as a polysodium salt with sodium chloride as a diluent. It proved a very effective sequestering agent in borate-containing developers. Whereas unmodified Kodak Developer D-76 precipitated on the addition of 40 mg. of calcium to a liter of the developer, the addition of 2 grams of the above agent per liter of D-76 prevented the formation of a precipitate even when 400 mg. of calcium were added per liter, or 1100 mg. of calcium chloride. This concentration of calcium is in excess of that found even in very hard water supplies.

#### EXAMPLE 7.—1,6-HEXANEDIAMINE-N,N',N',N'-TETRAMETHYLENEPHOSPHONIC ACID

This compound was prepared by the methods described previously and obtained as a polysodium salt with sodium chloride as a diluent. The calcium sequestering action was determined in a solution containing sulfite and borate as the precipitating ions in the proportions of 5 grams of anhydrous sodium sulfite, 0.75 gram of sodium bisulfite, and 2 grams of sodium metaborate octahydrate per 100 ml. The addition of 0.1 ml. of a 2.75 percent calcium chloride solution (containing 10 mg. of calcium per ml.) to 10 ml. of this solution caused the formation of a white precipitate, presumably of calcium sulfite and borate. But when 0.1 g. of the above compound was added to 10 ml. of this solution, 1.2 ml. of the calcium chloride solution were required to form a precipitate. The sequestering action was, therefore, in excess of 100 mg. of calcium or 275 mg. of calcium chloride per gram of the sequestering agent. This quantity of calcium is in excess of that found in most water supplies.

The sequestering agents of our invention can be incorporated in dry developer compositions of the type described by Kridel et al. U.S. Patents 2,666,702 and 2,666,703, issued January 19, 1954; Wiitala et al. U.S. Patents 2,682,464, and 2,682,465, issued June 29, 1954; Henn et al. U.S. Patent 2,685,513, issued August 3, 1954, and Baxendale et al. U.S. Patent 2,816,026, issued December 10, 1957.

Our dry developer compositions contain developing agents commonly used for developing exposed silver halide in emulsion layers used for black-and-white photography, such as p-aminophenol derivatives, e.g., monomethyl-p-aminophenol sulfate, ascorbic acid, hydroquinone, substituted hydroquinone, or a 3-pyrazolidone developer. Our dry compositions contain an alkali, for example, sodium carbonate, potassium carbonate, trisodium phosphate, sodium pyroborate, sodium metaborate, sodium hydroxide, potassium hydroxide, etc. Our dry compositions can contain an alkali sulfite, for example, sodium

sulfite, potassium sulfite, etc.; an alkali bisulfite, for example, sodium bisulfite, potassium bisulfite, etc.; an alkali metabisulfite, for example, sodium metabisulfite, potassium metabisulfite, etc. Sufficient amounts of these dry materials are used to provide in a solution prepared from the composition from 0.1 to 50 grams per liter of the amino-N,N-dimethylenephosphonic acid sequestering agent.

For example, the following composition is packaged ready for dissolving in one liter of water to make a photographic developing solution:

Compartment A:	Grams
Monomethyl-p-aminophenol sulfate -----	5.0
Hydroquinone -----	2.5
Compartment B:	
Sodium sulfite (anhydrous) -----	60.0
Sodium metaborate -----	20.0
EDTM -----	10.0
Sodium hydroxide -----	30.0

If desired, the EDTMP can be placed in Compartment A rather than in Compartment B.

Other materials can be added to the dry developer compositions, such as antifoggants, e.g., benzotriazole, development restrainers, e.g., alkali bromides, etc.

Developing compositions containing the calcium sequestrants of this invention can be combined developing and fixing solutions or combined developing and stabilizing baths, e.g., monobaths, such as those disclosed in Haist et al. U.S. Patent 2,875,048, issued February 24, 1959, Dreywood U.S. Patent 2,525,532, issued October 10, 1950, King U.S. Patent 2,397,016, issued March 19, 1946, Goldhammer U.S. Patents 2,782,121 and 2,901,350, issued February 19, 1957 and August 25, 1959, respectively, and Goldhammer et al. U.S. Patent 2,782,120, issued February 19, 1957. Some of these combined developer and fixer, or developer and stabilizer compositions can be prepared in dry form for making working solutions later.

It is to be understood that, if desired, the incorporation of the amino-N,N-dimethylenephosphonic acid sequestering agent in the developer can be accomplished by adding the sequesterant to the emulsion layer or to a gelatin interlayer of a photographic element, and, as a result of treating the layer or interlayer with developing solution, the amino-N,N-dimethylenephosphonic acid will be thereby introduced into the photographic developer composition.

The sequestrants of our invention are not only useful for removing calcium ions, but also for magnesium or any other hard water cations which may be present in a developer solution.

The invention has been described in 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 hereinabove and as defined in the appended claims.

What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A photographic developer comprising an aqueous alkaline solution of a developing agent for photoexposed silver halide and a water-soluble salt of an acid selected from the class consisting of ethylenediamine-N,N,N',N'-

tetramethylenephosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, 1,2-cyclohexanediamine-N,N,N',N'-tetramethylenephosphonic acid, o-carboxyanilino-N,N-dimethylenephosphonic acid, 1,3-diaminopropanol-N,N,N',N'-tetramethylenephosphonic acid, 1,3-propanediamine-N,N,N',N'-tetramethylenephosphonic acid, 1,6-hexanediamine-N,N,N',N'-tetramethylenephosphonic acid, 2-pyridylamino-N,N'-dimethylenephosphonic acid and a compound represented by the following general formula:



wherein R represents a group selected from the class consisting of alkyl containing from 1 to 4 carbon atoms, aryl containing from 6 to 7 carbon atoms, aralkyl containing from 7 to 9 carbon atoms, cyclohexyl, cyclopentyl, pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl and tetrahydroquinolylmethyl.

2. A photographic developer as defined in claim 1 wherein the developing agent is a polyhydroxybenzene.

3. A photographic developer as defined in claim 1 wherein the developing agent is a 3-pyrazolidone.

4. A photographic developer as defined in claim 1 wherein the developing agent is a monoalkyl-p-aminophenol.

5. A photographic developer as defined in claim 1 wherein said aqueous alkaline solution contains a silver halide solvent.

6. A photographic developer comprising an aqueous alkaline solution of a developing agent for photoexposed silver halide and a water-soluble salt of ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid.

7. A photographic developer comprising an aqueous alkaline solution of a developing agent for photoexposed silver halide and a water-soluble salt of 1,3-diamino-2-propanol-N,N,N',N'-tetramethylene-phosphonic acid.

8. A photographic developer comprising an aqueous alkaline solution of a developing agent for photoexposed silver halide and a water-soluble salt of nitrilo-N,N,N-trimethylenephosphonic acid.

9. A photographic developer comprising an aqueous alkaline solution of a developing agent for photoexposed silver halide and a water-soluble salt of propylamino-N,N-dimethylenephosphonic acid.

10. A photographic developer comprising an aqueous alkaline solution of a developing agent for photoexposed silver halide and a water-soluble salt of o-carboxyanilino-N,N-dimethylenephosphonic acid.

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NORMAN G. TORCHIN, *Primary Examiner*.

PHILIP E. MANGAN, *Examiner*.