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PATENT SPECIFICATION

NO DRAWINGS

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Int. Cl.:—G 03 c

COMPLETE SPECIFICATION

Photographic Developing and other processing Compositions

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, 343 State Street, Rochester 4, New York, United States of America, (Assignees of CHARLES FRANCIS HITCHCOCK ALLEN, JOHN ALBERT FORD and RICHARD WINTHROP HENN) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to photographic processing (especially developing) compositions containing metal precipitation inhibitors.

Most silver halide photographic developing solutions contain anions, such as carbonate, sulphite, 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, sulphites, 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, it has been suggested to include alkali hexametaphosphates and polyphosphates, e.g., alkali tetraphosphates, in developing solutions to reduce the formation of the calcium sulphite 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

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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 aluminium phosphate.

Some acids, such as citric, tartaric, gluconic and diglycolic acids, 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 sequestrants in developing solutions has also been previously disclosed. Some of these, such as ethylenediaminetetracetic 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% of one of these materials, together with 8 p.p.m. of iron and 2 p.p.m. of copper, will cause 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 bromoiodide types.

According to the present invention, there is provided a photographic processing composition (as herein defined) containing as a sequestering agent an amino-N,N-dimethylene-phosphonic acid or a water-soluble salt thereof.

The invention is particularly useful when applied to developing solutions, but may also be applied to photographic fixing, toning and bleach compositions, where calcium or other metal precipitates can occur and pose a problem.

Developing solutions prepared according to the invention are found to have good stability, high sequestering potency, low fogging propensity, and little or no tendency to promote developer oxidation even when traces of iron

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or other materials are present. In particular, the formation of calcium containing sludges, scums, and scales in developing solution.

The amino - N,N - dimethylenephosphonic acids and their water-soluble salts which may be employed in the present invention include those represented by the following general formula:



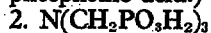
wherein M represents a hydrogen atom or a cation which imparts water solubility, such as an alkali metal (e.g. sodium or potassium), ammonium, pyridinium, triethanol ammonium or triethyl ammonium, and R represents an alkyl group such as one containing from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl or butyl, an aryl group such as phenyl, *o*-, *m*- or *p*-tolyl, *o*- or *p*-carboxyphenyl (or a water-soluble salt thereof, such as the sodium or potassium salt), an aralkyl group, such as benzyl, β -phenethyl or *o*-acetamidobenzyl (particularly an aralkyl group containing from 7 to 9 carbon atoms), an alicyclic group containing from 5 to 6 carbon atoms, such as cyclohexyl or cyclopentyl, or a heterocyclic radical, such as a heterocyclylalkyl

group (e.g. pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl or tetrahydroquinolylmethyl). The R group of Formula I above can be further substituted (especially where R represents an alkyl group) with a radical, such as hydroxyl, $-N(CH_2PO_3M_2)_2$, where M has the values given above, chlorine or alkoxy (e.g. methoxyl or ethoxyl).

As indicated above, the amino-N,N-dimethylenephosphonic acids 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 is formed. The sequestering agents of the present invention may be prepared according to the procedures of Specification No. 703,181. This method comprises reacting a chloromethylenephosphonic acid with an organic amine. Alternatively, the 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 include the following:

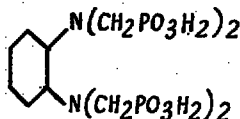


ethylenediamine - N,N,N',N' - tetramethylenephosphonic acid (EDTMP) (Prepared from ethylenediamine and chloromethylenephosphonic acid.)



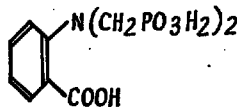
nitriolo - N,N,N - trimethylenephosphonic acid (Prepared from ammonia and chloromethylenephosphonic acid.)

3.

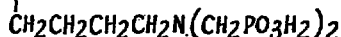


1,2 - cyclohexanediamine - N,N,N',N' - tetramethylenephosphonic acid (Prepared from 1,2 - diaminocyclohexane and chloromethylenephosphonic acid.)

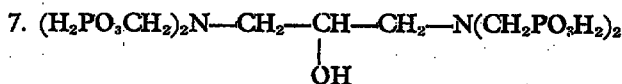
4.



6.



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



1,3 - diaminopropanol - N,N,N',N' - tetramethylenephosphonic acid (DPTP) (Pre-

pared from 1,3 - diaminopropan - 2 - ol and chloromethylenephosphonic acid.)



1,3 - propanediamine - N,N,N',N' - tetramethylenephosphonic acid (Prepared from

1,3 - propanediamine and chloromethylenephosphonic acid.)

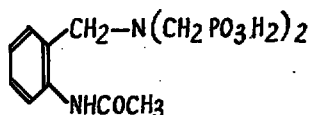
heterocyclyl alkyl



9. $(\text{H}_2\text{PO}_3\text{CH}_2)_2\text{N}-(\text{CH}_2)_6-\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$

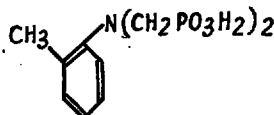
1,6 - hexanediamine - $\text{N},\text{N},\text{N}',\text{N}'$ - tetramethylenephosphonic acid (Prepared from 1,6 - hexanediamine and chloromethylenephosphonic acid.)

10.



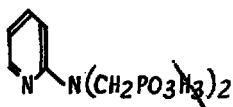
o - acetamidobenzylamino - N,N - dimethylenephosphonic acid (Prepared from *o* - acetamidobenzylamine and chloromethylenephosphonic acid.)

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 can be employed in photographic developing solutions of the type normally employed in black-and-white photography, or in colour photography. They can also be employed in photographic solutions which are intended for use in the removal or stabilisation of unexposed silver halide such as in fixing or stabilising solutions, or they can be added to toning or bleach 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 and methylhydroquinone, monoalkylaminophenols, such as *N*-methyl-*p*-aminophenol (sulphate or hydrochloride), 3-pyrazolidones, such as 1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone and 4,4 - diethyl - 1 - phenyl - 3-pyrazolidone.

40 pyrazolidone.

The colour-forming developers useful in the invention have been previously described in the prior art and the invention is not restricted to the use of any particular colour-forming developer. Particularly useful colour-forming developers are the phenylenediamines and substituted derivatives thereof. Typical of such colour-forming developers are the sulphonamido - substituted *p* - phenylenediamines disclosed in Specifications Nos. 651,749; 653,284; and 663,101. Other phenylenediamine colour-forming developing agents can be employed in the developing solutions of the invention.

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

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

The following examples illustrate the present invention.

EXAMPLE 1.

Calcium Sequestering Ability

The effectiveness of ethylenediamine - $\text{N},\text{N},\text{N}',\text{N}'$ - tetramethylenephosphonic acid (EDTMP) as a sequestering agent against carbonate ion was determined by employing a 2.5% aqueous solution of sodium sesquicarbonate, $\text{Na}_2\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$, which buffers in the pH region of 10.0, common to photographic developers. The solution without further addition was used as a control, the tetra sodium 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% pure, the diluent comprising sodium chloride. A 1% aqueous calcium chloride solution was added to this until a permanent precipitate was produced. The following values were established:

Addendum	Concentration		CaCl ₂ to Produce Ppt. Mg. per Litre
	Grams per Litre	Mols per Litre	
Control	—	—	50
EDTA . 2H ₂ O (tetra-sodium salt)	5	0.012	1400
EDTMP (hepta-sodium salt)	10	0.0127	1100

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 resistance to aerial fog and so reduce its useful life, for example, by 10 to 30%. However, the further addition of an aminocarboxylic acid complexing agent, such as ethylenediaminetetracetic acid (EDTA), will cause rapid oxidation, reducing the life to perhaps 10 to 20% 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 discoloured about ten times 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

Addendum	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*	0.96	—	—	1.10	0.10
EDTA					
Hue	Clear	Med. Brown	Very Dark	—	—
Activity*	0.92	0.78	0.00	—	—
EDTMP					
Hue	Clear	Clear	Clear	Clear	Med. Brown
Activity*	0.95	—	—	1.10	0.94

* 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- <i>p</i> -aminophenol sulphate	2.0 grams
Sodium sulphite, desiccated	100.0 "
Hydroquinone	5.0 "
Sodium tetraborate (10H ₂ O)	2.0 "
Water to make	1.0 litre

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 of the above composition is compared with the same developer modified by the addition of 2

grams of the EDTMP, heptasodium salt, per litre. 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 litre	0.73
EDTMP, 10 grams per litre	0.15

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

Monomethyl-p-aminophenol sulphate	2.5 grams
Sodium sulphite, desiccated	30.0 "
Hydroquinone	2.5 "
Sodium metaborate $\cdot 8\text{H}_2\text{O}$	10.0 "
Potassium bromide	0.5 "
Water to make	1.0 litre

EXAMPLE 5.

1,3 - Diaminopropan - 2 - ol tetramethylene-phosphonic acid (DPTP)

This material was prepared by reacting 1,3-diaminopropan - 2 - ol with chloromethylene-phosphonic acid. The reaction product contained about 50% by weight of the octasodium salt of the sequestrant and about 50% of sodium chloride. It proved to be an effective sequestering agent when employed under the conditions of Example 1, sequestering 100 mgs. 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 - $\text{N},\text{N},\text{N}',\text{N}'$ - 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 mgs. of calcium to one litre of the developer, the



addition of 2 grams of the above agent per litre of D-76 prevented the formation of a precipitate even when 400 mgs. of calcium were added per litre, equivalent to 1100 mgs. 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,N¹,N¹ - 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 sulphite and borate as the precipitating ions in the proportions of 5 grams of anhydrous sodium sulphite, 0.75 gram of sodium bisulphite, and 2 grams of sodium metaborate octahydrate per 100 mls. The addition of 0.1 ml. of 2.75% calcium chloride solution (containing 10 mgs. of calcium per ml.) to 10 mls. of this solution caused the formation of a white precipitate, presumably of calcium sulphite and borate. But when 0.1 gram of the tetramethylenephosphonic acid was added to 10 mls. of this solution, 1.2 mls. of the calcium chloride solution were required to form a precipitate. The sequestering action was, therefore, in excess of 100 mgs. of calcium or 275 mgs. 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 in Specifications Nos. 729,388; 729,862; 731,407; 731,419; and 732,945 and U.S. Patent 2,816,026.

The invention includes dry developer compositions containing developing agents commonly used for developing exposed silver halide grains in emulsion layers used for black-and-white photography, such as *p*-aminophenol derivatives, e.g. N - monomethyl - *p*-aminophenol sulphate, ascorbic acid, hydroquinone, substituted hydroquinone, or a 3-pyrazolidone developer. The dry compositions contain an alkali, for example, sodium carbonate, potassium carbonate, trisodium phosphate, sodium pyroborate, sodium metaborate, sodium hydroxide, or potassium hydroxide and can contain an alkali sulphite, for example, sodium or potassium sulphite, an alkali bisulphite, for example, sodium or potassium bisulphite, an alkali metabisulphite, for example sodium or potassium metabisulphite. The dry compositions contain sufficient amino - N,N - dimethylenephosphonic acid sequestering agent to provide from 0.1 to 50 grams per litre of the compound.

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

Compartment A

N-Monomethyl- <i>p</i> -aminophenol sulphate	5.0 grams
Hydroquinone	2.5 "

Compartment B

Sodium sulphite (anhydrous)	60.0 grams
Sodium metaborate	20.0 "
EDTMP	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, and development restrainers, e.g. alkali bromides.

Developing compositions containing the sequestrants of this invention can be combined developing and fixing solutions or combined developing and stabilising baths, e.g., monobaths, such as those disclosed in Specifications Nos. 631,184, 765,250 and 898,328. Some of these combined developer and fixer,

or developer and stabilizer compositions can be prepared in dry form for making working solutions later.

5 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.

15 The sequestrants of the present 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.

20 The word "Kodak" employed hereinabove is a Registered Trade Mark.

The terms "photographic processing compositions" and "photographic processing solutions" as employed in this specification, refer to photographic developing, fixing, toning or bleach compositions and solutions respectively, and include combined developing and fixing compositions and solutions.

WHAT WE CLAIM IS:—

30 1. A photographic dry processing composition (as herein defined) containing an amino - N,N - dimethylenephosphonic acid or a water-soluble salt thereof in sufficient amount to act as sequestering compound when the composition is dissolved in water.

35 2. A processing composition as claimed in Claim 1, in which the amino - N,N - dimethylenephosphonic acid has the general formula



40 wherein M represents hydrogen or a water-solubilizing cation and R represents an alkyl (including substituted alkyl), aryl, aralkyl, alicyclic, or heterocyclalkyl group.

3. A processing composition as claimed in Claim 2, in which the amino - N,N - dimethylenephosphonic acid is one of compounds 1, 2, 4, 5 and 7 hereinbefore specified.

4. A photographic processing solution comprising an aqueous solution of the composition as claimed in any of the preceding claims.

5. A processing solution as claimed in Claim 4, in which the concentration of the amino - N,N - dimethylenephosphonic acid is between 0.1 and 50 grams per litre.

6. A processing solution as claimed in Claim 5, in which the said concentration is between 0.5 and 10 grams per litre.

7. A photographic developing solution or dry composition comprising a processing solution according to Claims 4 to 6 or dry composition according to Claims 1 to 3 also containing a photographic silver halide developing agent.

8. A developing solution or composition according to Claim 7, in which the developing agent is one or more of the following:

a polyhydroxybenzene developing agent,
a 3-pyrazolidone developing agent,
an N - monoalkyl - *p*-aminophenol developing agent.

9. A developing solution or composition according to either Claim 7 or 8, also containing a silver halide solvent.

10. Photographic processing solutions according to Claim 4 and photographic dry processing compositions according to Claim 1 substantially as herein described.

11. A method of processing an exposed photographic silver halide emulsion layer which comprises performing a developing, fixing, toning or bleaching step in the presence of sufficient amino - N,N - dimethylenephosphonic acid or a water-soluble salt thereof, to act as a sequestering compound.

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Patent Agent.

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 sequestrant 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 the present 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.

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The terms "photographic processing compositions" and "photographic processing solutions" as employed in this specification, refer to photographic developing, fixing, toning or bleach compositions and solutions respectively, and include combined developing and fixing compositions and solutions.

WHAT WE CLAIM IS:—

1. A photographic dry processing composition (as herein defined) containing an amino - N,N - dimethylenephosphonic acid or a water-soluble salt thereof in sufficient amount to act as sequestering compound when the composition is dissolved in water.

2. A processing composition as claimed in Claim 1, in which the amino - N,N - dimethylenephosphonic acid has the general formula



wherein M represents hydrogen or a water-solubilizing cation and R represents an alkyl (including substituted alkyl), aryl, aralkyl, alicyclic, or heterocyclylalkyl group.

3. A processing composition as claimed in Claim 2, in which the amino - N,N - dimethylenephosphonic acid is one of compounds 1, 2, 4, 5 and 7 hereinbefore specified.

4. A photographic processing solution comprising an aqueous solution of the composition as claimed in any of the preceding claims.

5. A processing solution as claimed in Claim 4, in which the concentration of the amino - N,N - dimethylenephosphonic acid is between 0.1 and 50 grams per litre.

6. A processing solution as claimed in Claim 5, in which the said concentration is between 0.5 and 10 grams per litre.

7. A photographic developing solution or dry composition comprising a processing solution according to Claims 4 to 6 or dry composition according to Claims 1 to 3 also containing a photographic silver halide developing agent.

8. A developing solution or composition according to Claim 7, in which the developing agent is one or more of the following:

a polyhydroxybenzene developing agent,

a 3-pyrazolidone developing agent,

an N - monoalkyl - *p*-aminophenol developing agent.

9. A developing solution or composition according to either Claim 7 or 8, also containing a silver halide solvent.

10. Photographic processing solutions according to Claim 4 and photographic dry processing compositions according to Claim 1 substantially as herein described.

11. A method of processing an exposed photographic silver halide emulsion layer which comprises performing a developing, fixing, toning or bleaching step in the presence of sufficient amino - N,N - dimethylenephosphonic acid or a water-soluble salt thereof, to act as a sequestering compound.

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