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DETERGENT COMPOSITIONS CONTAINING METHANE TRI AND TETRA PHOSPHONIC ACID COMPOUNDS

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ABSTRACT OF THE DISCLOSURE

Compositions are prepared containing a detergent and a methane tri phosphonic acid, methane tetra phosphonic acid, halo methane tri phosphonic acid or an alkali metal or ammonium salt of such acids. Conventional phosphate builders can be included with the tri and tetra phosphonic acid compounds, and the tri and tetra phosphonates reduce the tendency of poly-phosphate builders toward reversion.

This invention relates to novel detergent compositions and to novel polyphosphonic acids and salts thereof.

It has been proposed in the past to employ methane diphosphonic acid and its alkali metal salts in detergent compositions (Orthner, German Patent 1,045,373, Dec. 4, 1958). Unfortunately, however, methane diphosphonic acid and its salts are relatively expensive to produce. While methane diphosphonic acid is a good builder and calcium sequestering agent, these properties can be improved upon. It is also desirable to have increased solubility in the sequestering agent.

It is an object of the present invention to prepare improved detergent compositions.

Another object is to prepare detergent compositions containing a phosphorus compound having a greater binding power for calcium ions than either alkali metal pyrophosphates or alkali metal tripolyphosphates.

An additional object is to prepare detergent compositions containing polyphosphates having a reduced tendency to revert to phosphoric acid.

Another object is to develop detergent compositions containing phosphonates superior to methane diphosphonic acid and its salts as sequestering agents for calcium ions.

A further object is to prepare phosphonate containing detergent compositions having improved stability.

Yet another object is to prepare detergent compositions having improved ability to remove sebum stains.

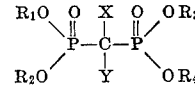
A still further object is to prepare phosphonate containing detergent compositions wherein the phosphonte has a lower surface tension than methane diphosphonic acid and its salts.

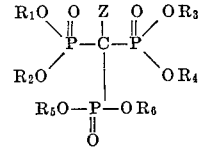
Another object is to prepare detergent compositions containing alkali metal phosphonates more nearly neutral than the alkali metal salts of methane diphosphonic acid.

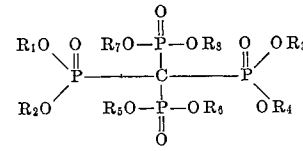
Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by employing detergent compositions containing poly-

phosphonic acids and/or alkali metal and ammonium salts thereof having one of the formulae

[I] 

[II] 

[III] 

where R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are the same or different and are selected from the group consisting of hydrogen, alkali metal (e.g., sodium, potassium, lithium, rubidium or cesium) or ammonium; X is selected from the group consisting of hydrogen, alkyl, alkenyl, chlorine, bromine, aryl (e.g., phenyl or alkylphenyl), chloroalkyl or chloroaryl (e.g., chlorophenyl); Y is selected from the group consisting of hydroxyl, phenyl, chlorine and bromine and Z is selected from the group consisting of phenyl, hydrogen, chlorine and bromine.

Examples of phosphonic acids and their salts useful in the detergent compositions of the present invention are chloromethane diphosphonic acid, dichloromethane diphosphonic acid, bromomethane diphosphonic acid, dibromomethane diphosphonic acid, chloromethane triphosphonic acid, bromomethane triphosphonic acid, methane triphosphonic acid, methane tetraphosphonic acid, hydroxymethane diphosphonic acid, methyl hydroxymethane diphosphonic acid (also called methyl hydroxymethylene diphosphonic acid or 1-methyl-1-hydroxymethane diphosphonic acid), ethyl hydroxymethane diphosphonic acid, butyl hydroxymethane diphosphonic acid, propyl hydroxymethane diphosphonic acid, isopropyl hydroxymethane diphosphonic acid, pentyl hydroxymethane diphosphonic acid, hexyl hydroxymethane diphosphonic acid, heptyl hydroxymethane diphosphonic acid, isoheptyl hydroxymethane diphosphonic acid, octyl hydroxymethane diphosphonic acid, nonyl hydroxymethane diphosphonic acid, decyl hydroxymethane diphosphonic acid, undecyl hydroxymethane diphosphonic acid, dodecyl hydroxymethane diphosphonic acid, tridecyl hydroxymethane diphosphonic acid, tetradecyl hydroxymethane diphosphonic acid, pentadecyl hydroxymethane diphosphonic acid, heptadecyl hydroxymethane diphosphonic acid, octadecyl hydroxymethane diphosphonic acid, nonadecyl hydroxymethane diphosphonic acid, heptadecenyl hydroxymethane diphosphonic acid, vinyl hydroxymethane diphosphonic acid, isopropenyl hydroxymethane diphosphonic acid, chloromethyl hydroxymethane diphosphonic acid, dichloromethyl hydroxymethane diphosphonic acid, trichloromethyl hydroxymethane diphosphonic acid, phenyl hydroxymethane diphosphonic acid, phenyl methane diphosphonic acid, phenyl methane triphosphonic acid, naphthyl hydroxy methane diphosphonic acid, p-chlorophenyl hydroxy methane diphosphonic acid, 2,4,5-trichlorophenyl hydroxy methane diphosphonic acid, 2,4,6-trichlorophenyl hydroxy methane diphosphonic acid, isononyl hydroxy methane diphosphonic acid and the

alkali metal and ammonium salts of such phosphonic acids.

Since the phosphonic acids used in the present invention have 4, 6 or 8 acidic hydrogen atoms (Formulae I, II and III respectively) in making the salts one or more of the acidic hydrogen atoms can be replaced by the alkali metal or ammonium ion in forming the salts. Usually all of the acidic hydrogen atoms are replaced in making the salt and unless otherwise indicated when reference is made to a salt in the present specification, all of the acidic hydrogen atoms are replaced. However, it should be understood that this is not an essential part of the present invention and the invention includes the use of the partial as well as the complete salts, e.g., monosodium methane tetraphosphonate, disodium methane tetraphosphonate, trisodium methane tetraphosphonate, tetrasodium methane tetraphosphonate, pentasodium methane tetraphosphonate, hexasodium methane tetraphosphonate, heptasodium methane tetraphosphonate, octasodium methane tetraphosphonate, mono potassium methane tetraphosphonate, tetra potassium methane tetraphosphonate, octa potassium methane tetraphosphonate, mono ammonium methane tetraphosphonate, octa ammonium methane tetraphosphonate, monosodium methane triphosphonate, trisodium methane triphosphonate, pentasodium methane triphosphonate, hexasodium methane triphosphonate, dipotassium methane triphosphonate, tetra potassium methane triphosphonate, hexa potassium methane triphosphonate, mono ammonium methane triphosphonate, hexa ammonium methane triphosphonate, monosodium chloromethane triphosphonate, tetrasodium chloromethane triphosphonate, hexasodium chloromethane triphosphonate, mono potassium chloromethane triphosphonate, tri ammonium chloromethane triphosphonate, hexa ammonium chloromethane triphosphonate, monosodium chloromethane diphosphonate, disodium chloromethane diphosphonate, trisodium chloromethane diphosphonate, tetrasodium chloromethane diphosphonate, mono potassium chloromethane diphosphonate, tetra potassium chloromethane diphosphonate, di ammonium chloromethane diphosphonate, tetra ammonium chloromethane diphosphonate, monosodium dichloromethane diphosphonate, disodium dichloromehane diphosphonate, tetrasodium dichloromethane diphosphonate, tri potassium dichloromethane diphosphonate, tetra potassium dichloromethane diphosphonate, mono ammonium dichloromethane diphosphonate, tetra ammonium dichloromethane diphosphonate, monosodium phenyl methane triphosphonate, trisodium phenyl methane triphosphonate, hexasodium phenyl methane triphosphonate, tetrapotassium phenyl methane triphosphonate, hexa potassium phenyl methane triphosphonate, hexa ammonium phenyl methane triphosphonate, tetrasodium hydroxymethane diphosphonate, monosodium methyl hydroxymethane diphosphonate, disodium methyl hydroxymethane diphosphonate, trisodium methyl hydroxymethane diphosphonate, tetrasodium methyl hydroxymethane diphosphonate, potassium methyl hydroxymethane diphosphonate, tetra potassium methyl hydroxymethane diphosphonate, diammonium methyl hydroxymethane diphosphonate, tetra ammonium methyl hydroxymethane diphosphonate, monosodium ethyl hydroxymethane diphosphonate, tetrasodium ethyl hydroxymethane diphosphonate, tri potassium ethyl hydroxymethane diphosphonate, tetra ammonium ethyl hydroxymethane diphosphonate, monosodium propyl hydroxymethane diphosphonate, tetrasodium propyl hydroxymethane diphosphonate, dipotassium propyl hydroxymethane diphosphonate, tri ammonium propyl hydroxymethane diphosphonate, disodium isopropyl hydroxymethane diphosphonate, tetra potassium isopropyl hydroxymethane diphosphonate, monosodium chloromethyl hydroxymethane diphosphonate, tetrasodium dichloromethyl hydroxymethane diphosphonate, tetrasodium chloromethyl hydroxymethane diphosphonate, mono potassium chloromethyl hydroxymethane diphosphonate, di potassium chloromethyl hydroxymethane diphosphonate, tetra ammonium chloromethyl hydroxymethane diphosphonate, mono potassium dichloromethyl hydroxymethane diphosphonate, monosodium trichloromethyl hydroxymethane diphosphonate, disodium trichloromethyl hydroxymethane diphosphonate, tetrasodium trichloromethyl hydroxymethane diphosphonate, mono potassium trichloromethyl hydroxymethane diphosphonate, tetra potasium trichloromethyl hydroxymethane diphosphonate, diammonium trichloromethyl hydroxymethane diphosphonate, tetrasodium butyl hydroxymethane diphosphonate, tri potassium butyl hydroxymethane diphosphonate, mono ammonium butyl hydroxymethane diphosphonate, monosodium pentyl hydroxymethane diphosphonate, tetrasodium pentyl hydroxymethane diphosphonate, di potassium pentyl hydroxymethane diphosphonate, monosodium hexyl hydroxymethane diphosphonate, trisodium hexyl hydroxymethane diphosphonate, tetrasodium hexyl hydroxymethane diphosphonate, tetra potassium hexyl hydroxymethane diphosphonate, tetra ammonium hexyl hydroxymethane diphosphonate, tetrasodium heptyl hydroxymethane diphosphonate, disodium heptyl hydroxymethane diphosphonate, mono potassium heptyl hydroxymethane diphosphonate, tri ammonium heptyl hydroxymethane diphosphonate, monosodium octyl hydroxymethane diphosphonate, trisodium octyl hydroxymethane diphosphonate, tetrasodium octyl hydroxymethane diphosphonate, tetra potassium octyl hydroxymethane diphosphonate, tetrasodium nonyl hydroxymethane diphosphonate, tetra ammonium octyl hydroxymethane diphosphonate, tetra potassium nonyl hydroxymethane diphosphonate, tetra ammonium nonyl hydroxymethane diphosphonate, disodium nonyl hydroxymethane diphosphonate, tetrasodium decyl hydroxymethane diphosphonate, di potassium decyl hydroxymethane diphosphonate, mono ammonium decyl hydroxymethane diphosphonate, monosodium isononyl hydroxymethane diphosphonate, tetrasodium isononyl hydroxymethane diphosponate, trisodium undecyl hydroxymethane diphosphonate, tetra potassium undecyl hydroxymethane diphosphonate, tetrasodium undecyl hydroxymethane diphosphonate, tetra ammonium undecyl hydroxymethane diphosphonate, tetrasodium dodecyl hydroxymethane diphosphonate, tetrasodium tridecyl hydroxymethane diphosphonate, tetra potassium tetradecyl hydroxymethane diphosphonate, monosodium pentadecyl hydroxymethane diphosphonate, trisodium pentadecyl hydroxymethane diphosphonate, tetrasodium pentadecyl hydroxymethane diphosphonate, di potassium pentadecyl hydroxymethane diphosphonate, tetra ammonium pentadecyl hydroxymethane diphosphonate, tetrasodium hexadecyl hydroxymethane diphosphonate, monosodium heptadecyl hydroxymethane diphosphonate, disodium heptadecyl hydroxymethane diphosphonate, trisodium heptadecyl hydroxy methane diphosphate, tetrasodium heptadecyl hydroxymethane diphosphonate, mono potassium heptadecyl hydroxymethane diphosphonate, tetra potassium heptadecyl hydroxymethane diphosphonate, mono ammonium heptadecyl hydroxymethane diphosphonate, tetrasodium octadecyl hydroxymethane diphosphonate, tetra sodium nonadecyl hydroxymethane diphosphonate, tetra potassium nonadecyl hydroxymethane diphosphonate, tetra ammonium nonadecyl hydroxymethane diphosphonate, tetrasodium vinyl hydroxymethane diphosphonate, tetra potassium isopropyl hydroxymethane diphosphonate, monosodium heptadecenyl hydroxymethane diphosphonate, disodium heptadecyl hydroxymethane diphosphonate, trisodium heptadecenyl hydroxymethane diphosphonate, tetrasodium heptadecenyl hydroxymethane diphosphonate, mono potassium heptadecenyl hydroxymethane diphosphonate, tetra potassium heptadecenyl hydroxymethane diphosphonate, di ammonium heptadecenyl hydroxymethane diphosphonate, tetra ammonium heptadecenyl hydroxymethane, diphos-

phonate, tetrasodium naphthyl hydroxymethane diphosphonate, monosodium phenyl hydroxymethane diphosphonate, disodium phenyl hydroxymethane diphosphonate, trisodium phenyl hydroxymethane diphosphonate, tetrasodium phenyl hydroxymethane diphosphonate, di potassium phenyl hydroxymethane diphosphonate, tetra potassium phenyl hydroxymethane diphosphonate, tetra ammonium phenyl hydroxymethane diphosphonate, monosodium phenyl methane diphosphonate, disodium phenyl methane diphosphonate, trisodium phenyl methane diphosphonate, tetrasodium phenyl methane diphosphonate, tetra potassium phenyl methane diphosphonate, tetra ammonium phenyl methane diphosphonate, tetrasodium p-chlorophenyl hydroxymethane diphosphonate, tetrasodium 2,4,5-trichlorophenyl hydroxymethane diphosphonate, tetra potassium 2,4,6-trichlorophenyl hydroxymethane diphosphonate.

Some of the polyphosphonic acids and salts employed in the present invention are old as shown for example, in Blaser Patent 3,122,417 and Schiefer Patent 3,149,151. In general the acids and salts can be prepared by the methods shown in Schiefer. Many of the free acids can also be formed by hydrolyzing the corresponding esters such as the esters shown in Schmidt Patent 2,848,475, for example. Preferably a lower alkyl ester is employed for such a hydrolysis and aqueous hydrochloric acid is used as the hydrolyzing agent as is illustrated infra. In such case the alkali metal or ammonium salts are formed by dissolving the free acid in aqueous sodium hydroxide or potassium hydroxide or ammonium hydroxide and evaporating to dryness, e.g., by spray drying. Sufficient alkali is employed to neutralize from one up to all the acid groups available on the phosphonic acid. The free methane triphosphonic acid, methane tetraphosphonic acid, chloromethane triphosphonic acid, chloromethane diphosphonic acid and dichloromethane diphosphonic acid and their salts can be prepared in the manner set forth in my copending application Ser. No. 482,257, filed Aug. 24, 1965.

The methane triphosphonic acid, methane tetraphosphonic acid, chloromethane triphosphonic acid and phenyl methane triphosphonic acid and their alkali metal salts are better phosphonic acid builders in the detergent compositions than methane diphosphonic acid and its alkali metal salts and also sequester more calcium and magnesium ions, for example than does methane diphosphonic acid or its alkali metal salts. The alkali metal salts also are more nearly neutral since the tri- and tetraphosphonic acids are stronger acids than methane diphosphonic acids.

The hydroxy containing methane diphosphonic acids and alkali metal salts of the present invention, e.g., methyl hydroxymethane diphosphonic acid and phenyl hydroxymethane diphosphonic acid and their alkali metal salts, have better solubility than the corresponding methane diphosphonic acid or its salts. Additionally the hydroxy containing compounds have better stability and complex formation properties due to hydrogen bonding available through the hydroxyl hydrogen. The chlorine containing polyphosphonic acids (and salts) used in the present invention have improved sebum stain removing properties than the corresponding methane diphosphonic acid (and salts).

The alkyl and alkenyl methane diphosphonic acids (and salts) having at least 8 carbon atoms in the alkyl or alkenyl group have surface activity and lower surface tension properties in their own right which are not exhibited by methane diphosphonic acid or lower alkyl or alkenyl methane diphosphonic acids (or their salts). Preferably the alkyl group has at least 10 carbon atoms, most preferably at least 12 carbon atoms.

The aryl methane diphosphonic acids (and salts) also exhibit these lower surface tension and surface activity properties. The aryl containing compounds, e.g., phenyl methane diphosphonic acid, phenyl hydroxymethane diphosphonic acid and phenyl methane triphosphonic acid (and their salts) are superior for metal extraction, e.g., extraction of gold, silver, vanadium, molybdenum, copper, nickel and iron.

All of the polyphosphonic acids (and salts) of the present invention are valuable in prevention of the reversion of polyphosphates, e.g., sodium tripolyphosphate, and pyrophosphates, e.g., tetra potassium pyrophosphate.

Unless otherwise indicated all parts and percentages are by weight.

The detergent compositions of the present invention normally contain 5–90% of detergent, usually 10–50%; and 10–80% of builder, usually 20–60%. The builder can be from 0.5–100% of the polyphosphonates (substituted methane) of the present invention with the balance being conventional phosphates, polyphosphates and pyrophosphates. If desired some methane diphosphonic acid or its alkali metal salts can be included.

Silicates can be used as corrosion inhibitors in an amount of 1–30%, usually 2–10% of the composition or they can be omitted. Borax can be added as a water softener in an amount of 1–40% or it can be omitted.

The detergents can be anionic, cationic or nonionic. Preferably they are anionic.

Examples of suitable detergents are sodium stearate (soap), sodium palmitate, sodium elaidate, potassium stearate, potassium oleate, sodium oleate, higher alkylaryl sulfonates containing 8–22 carbon atoms in the alkyl group, e.g., higher alkyl benzene sulfonates, higher alkyl toluene sulfonates and higher alkyl phenol sulfonates. Thus there can be used sodium decylbenzene sulfonate, sodium dodecyl benzene sulfonate, potassium dodecyl benzene sulfonate, sodium keryl sulfonate, sodium nonyl benzene sulfonate, sodium decylphenol sulfonate, potassium pentadecyl benzene sulfonate, ammonium dodecyl benzene sulfonate, triethanolamine decyl benzene sulfonate, monoethanolamine dodecyl toluene sulfonate, sodium octadecyl benzene sulfonate, diethanolamine tetradecyl benzene sulfonate. Normally the alkali metal salts, e.g., the sodium or potassium salts, of the higher alkyl aromatic sulfonic acids are used but as indicated ammonium or amine salts are used. The alkyl groups can be branched or straight chain depending upon the method of manufacturing the higher alkyl aromatic sulfonic acid as is well known in the art.

Other anionic detergents include normally and secondary higher alkyl sulfate detergents, particularly the alkali metal salts of such sulfates, those having 8 to 22 carbon atoms in the alkyl residue such as sodium lauryl sulfate, potassium lauryl sulfate, sodium octadecyl sulfate, sodium coconut fatty alcohol sulfate, sodium octanyl sulfate, sodium alkyl (C_{14}–C_{18}) sulfate, as well as the corresponding long chain aliphatic sulfonates, e.g., sodium octanyl sulfonate, sodium dodecyl sulfonate, sodium tetradecyl sulfonate, sodium octadecyl sulfonate, potassium dodecyl sulfonate, ammonium dodecyl sulfonate, sodium decyl sulfonate, higher alkyl ether sulfates, higher alkyl glyceryl ether sulfonates, higher alkyl phenol polyethylene oxide sulfates, polyoxyethyl ethers of fatty alcohols, polyethylene oxide condensates with higher alkyl phenols such as isooctyl and nonyl phenol condensed with 8 to 20 moles of ethylene oxide, preferably about 10, and polyethylene condensates with hydrophobic polypropylene glycols e.g., pluronic L-64, sodium o-xylene sulfonate, potassium xylene sulfonate, potassium tertiary octylbenzene sulfonate, potassium dodecyl toluene sulfonate, sodium p-xylene sulfonate, sodium propyl napthalene sulfonate, sodium butylnaphthalene sulfonate.

Suds builders can be added such as alkylolamides, e.g., alkyl (C_8–C_{18}) monoethanolamide, higher fatty alcohols, e.g., stearyl alcohol and oleyl alcohol, cationic detergents such as lauramidodipropyl dimethyl benzyl ammonium chloride and N-diethylamino oleylamide hydrochloride.

As indicated any of the conventional phosphate builders can be included and the polyphosphonates of the present invention reduce to the tendency of the polyphosphates toward reversion. Examples of phosphate builders are

sodium hexametaphosphate, sodium tripolyphosphate, tetrasodium pyrophosphate, trisodium phosphate tetrapotassium pyrophosphate, potassium tripolyphosphate, sodium and tripolyphosphate, pentapotassium tripolyphosphate.

Any of the conventional alkali metal silicate builders can also be employed in addition to or in place of the polyphosphates. Typical examples of suitable silicates have an alkali oxide to silica ratio within the range of from 1:1 to 1:4 and preferably from about 1:2 to 1:3. Examples are sodium silicates having an Na_2O to SiO_2 mole ratio of 1:2.35; 1:2.5, 1:3.2, 1:2.0; 1:1.6 and 1:1.

Borax and sodium carbonate can also be present and normally there is also present some sodium sulfate or potassium sulfate in the detergent.

Brighteners and other conventional additives to detergent composition can also be present. Thus there can be used polyvinyl alcohol (PVA) and carboxymethylcellulose (CMC).

Example 1

166.2 grams (1 mole) triethyl phosphite was added dropwise with stirring to 78.4 grams (1 mole) of acetyl chloride over a period of 30 minutes at a temperature of 30° to 35° C. maintained by cooling. Ethyl chloride was evolved. The temperature was increased to 60° C. over the next 1 hour and 15 minutes, at which time the evolution of ethyl chloride was complete. The product was distilled under vacuum yielding 176 grams of diethyl acetylphosphonate (DEAP) in 98% yield, B.P. about 80° C. at 5 mm. and havin ga refractive index of 1.4240 at 200° C.

Then to 118.3 grams (0.9 mole) of diethyl phosphite there were added 2.4 grams of sodium metal. The reaction was exothermic at about 60° C. when all the sodium had reacted. Then the DEAP was added dropwise over a 15 miunte period at 60° to 90° C. Heating was continued and the temperature held at 100° C. for an additional hour. The product was then distilled to give tetraethyl methyl hydroxymethane diphosphonate (also called tetraethyl 1-hydroxyethylidene diphosphonate) in a yield of 286 grams (90%) B.P. 150° to 160° C. at 1.5 mm. 0.9 mole of tetraethyl 1-hydroxyethylidene diphosphonate was refluxed with 5.4 moles of concentrated hydrochloric acid for 12 hours. Excess acid was removed by stripping under vacuum. 200 ml. of water were added and removed in vacuo, then finally, 200 ml. of benzene were added and the water removed and separated by means of a Dean and Starke trap and the benzene was distilled over under reduced pressure, yielding 184 grams (100% yield) of methyl hydroxymethane diphosphonic acid as a syrup having a neutralization equivalent of 1080 mg. KOH/gm. (Theory is 1087 mg. KOH/gm.); P 3.05% (Theory 3.01%); C 11.54% (Theory 11.65%); H 2.90% (Theory 2.94%).

Example 2

To 140.57 grams (1.0 mole) of benzoyl chloride at 90° C. there were added 166.2 grams (1.0 mole) of triethyl phosphite over a period of 1 hour. Ethyl chloride evolution ceased at the end of this period. The unreacted benzoyl chloride and triethyl phosphite were removed by distillation at reduced pressure, terminal conditions being 100° C. and 8 mm. leaving a residue of 236 grams (90% yield) of diethyl benzoylphosphonate which was reacted with diethyl sodium phosphite as in Example 1 to produce tetraethyl phenyl hydroxymethane diphosphonate. This was hydrolyzed and the hydrolysis product purified in the same manner as in Example 1 to produce phenyl hydroxymethane diphosphonic acid as a viscous syrup having an acid number of 822 mg. KOH/mg. (Theory is 836 mg. KOH/gm.); P 22.8% (Theory 22.9%).

Example 3

There were charged into the reaction vessel 23.0 grams (1.0 mole) of sodium metal along with 90 cc. of xylene and 80 cc. of tetrahydrofurane. The vessel was placed under a nitrogen blanket and 138.10 grams (1.0 mole) of diethyl phosphite added over a 35 minute period. An exothermic reaction ensued which was maintained at 62° C. by external cooling. After addition was complete the mixture was heated to 100° C. and held there until all of the sodium metal was gone. The mixture was cooled to 60° to 70° C. and 80.50 grams (0.5 mole) of benzal chloride were added gradually over a 25 minute period. An exothermic reaction ensued which was maintained at 60° to 70° C. by external cooling. The mixture was then heated for 4 hours at 70° to 75° C., cooling to 60° C. The liquid material was separated from the solid and the solid boiled 8 times with 100 cc. of benzene to extract the organic material. The eluate product was then distilled, terminal conditions being a pot temperature of 201° C., distillate temperature 125° C. and pressure 6 mm. The solid residue of 70 grams was tetraethyl phenyl methane diphosphonate. This product was hydrolyzed and the hydrolysis product purified as in Example 1 to obtain phenyl methane diphosphonic acid.

Example 4

There were mixed together 23.0 grams (1.0 mole) of sodium metal along with 90 cc. of xylene and 80 cc. of tetrahydrofurane and the mixture placed under a nitrogen atmosphere. There were then added over a 35 minute period 138.10 grams (1.0 mole) of diethyl phosphite using external cooling to control the reaction exotherm and maintain the temperature at 60° to 65° C. After addition was complete the mixture was heated to 100° C. and maintained there for about 1 hour until there was no more sodium. The mixture was cooled to 60° C. and there was started the addition of 64.5 grams (0.33 mole) of benzotrichloride (α,α,α-trichlorotoluene). The exothermic reaction was cooled to maintain the temperature at 60° to 65° C. during the 25 minute addition period. The mixture was heated at 70° to 75° C. for 7 hours and the sodium chloride filtered off. The product in the pot was then subjected to distillation, terminal conditions being a pot temperature of 205° C., distillate temperature 125° C. and pressure 4 mm. The solid residue in the pot was hexaethyl phenyl methane triphosphonate. This product was hydrolyzed and the hydrolysis product purified as in Example 1 to obtain phenyl methane triphosphonic acid.

Example 5

The procedure of Example 1 was repeated replacing the acetyl chloride by equal molar amounts of (a) propionyl chloride, (b) butyryl chloride, (c) isobutyryl chloride, (d) pentanoyl chloride, (e) caproyl chloride, (f) heptanoyl chloride, (g) octanoyl chloride, (h) nonanoyl chloride, (i) isodecanoyl chloride, (j) decanoyl chloride, (k) undecanoyl chloride, (l) dodecanoyl chloride, (m) tridecanoyl chloride, (n) hexadecanoyl chloride, (o) octadecanoyl chloride, (p) octadecenoyl chloride, (q) naphthanoyl chloride, (r) chloroacetyl chloride, (s) dichloroacetyl chloride and (t) trichloroacetyl chloride to produce as the resultant hydrolysis products (a) ethyl hydrorymethane diphosphonic acid, (b) propyl hydroxymethane diphosphonic acid, (c) isopropyl hydroxymethane diphosphonic acid, (d) butyl hydroxymethane diphosphonic acid, (e) pentyl hydroxymethane disphosphonic acid, (f) hexyl hydroxymethane diphosphonic acid, (g) heptyl hydroxymethane diphosphonic acid, (h) octyl hydroxymethane diphosphonic acid, (i) isononyl hydroxymethane diphosphonic acid, (j) nonyl hydroxymethane diphosphonic acid, (k) decyl hydroxymethane diphosphonic acid, (l) undecyl hydroxymethane diphosphonic acid, (m) dodecyl hydroxymethane diphosphonic acid, (n) pentadecyl hydroxymethane diphosphonic acid, (o) heptadecyl hydroxymethane diphosphonic acid, (p) heptadecenyl hydroxymethane diphosphonic acid, (q) napthyl hydroxymethane diphosphonic acid, (r) chloromethyl hydroxymethane diphosphonic acid, (s) dichloro-

methyl hydroxymethane diphosphonic acid and (t) trichloromethyl hydroxymethane diphosphonic acid.

Example 6

To 1 mole of methyl hydroxymethane diphosphonic acid there were added 4 moles of 10% aqueous sodium hydroxide and the mixture was evaporated to dryness to produce tetrasodium methyl hydroxymethane diphosphonate.

Example 7

To 1 mole of phenyl hydroxymethane diphosphonic acid there were added 4 moles of 10% aqueous sodium hydroxide and the mixture was evaporated to dryness to produce tetrasodium phenyl hydroxymethane diphosphonate.

Example 8

To 1 mole of phenyl methane diphosphonic acid there were added 4 moles of 10% aqueous sodium hydroxide and the mixture was evaporated to dryness to produce tetrasodium phenyl methane diphosphonate.

Example 9

To 1 mole of phenyl methane triphosphonic acid there were added 6 moles of 10% aqueous sodium hydroxide and the mixture was evaporated to dryness to produce hexasodium phenyl methane triphosphonate.

Example 10

The procedure of Example 6 was repeated replacing the methyl hydroxymethane diphosphonic acid by each of the diphosphonic acids prepared in Example 5 (a) through (t) to produce respectively, (a) tetrasodium ethyl hydroxymethane diphosphonate, (b) tetrasodium propyl hydroxymethane diphosphonate, (c) tetrasodium isopropyl hydroxymethane diphosphonate, (d) tetrasodium butyl hydroxymethane diphosphonate, (e) tetrasodium pentyl hydroxymethane diphosphonate, (f) tetrasodium hexyl hydroxymethane diphosphonate, (g) tetrasodium heptyl hydroxymethane diphosphonate, (h) tetrasodium octyl hydroxymethane diphosphonate, (i) tetrasodium isononyl hydroxymethane diphosphonate, (j) tetrasodium nonyl hydroxymethane diphosphonate, (k) tetrasodium decyl hydroxymethane diphosphonate, (l) tetrasodium undecyl hydroxymethane diphosphonate, (m) tetrasodium dodecyl hydroxymethane diphosphonate, (n) tetrasodium pentadecyl hydroxymethane diphosphonate, (o) tetrasodium heptadecyl hydroxymethane diphosphonate, (p) tetrasodium heptadecenyl hydroxymethane diphosphonate, (q) tetrasodium naphthyl hydroxymethane diphosphonate, (r) tetrasodium chloromethyl hydroxymethane diphosphonate, (s) tetrasodium dichloromethyl hydroxymethane diphosphonate, (t) tetrasodium trichloromethyl hydroxymethane diphosphonate. The corresponding potassium and ammonium salts can be prepared by replacing the 10% sodium hydroxide by an equal molar amount of 10% potassium hydroxide or ammonium hydroxide.

The following examples illustrate various detergent formulations.

Ultrawet H is potassium xylene sulfonate.

Example 11

The addition of 1% methyl hydroxymethane diphosphonic acid to sodium tripolyphosphate reduced its reversion to phosphate from 11% to 3% in boiling water over a 3 minute period. Similar results were obtained using 1% of tetrasodium methyl hydroxymethane disphosphonate. In place of the methyl hydroxymethane diphosphonic acid there can also be used in this example the same amount of (a) octyl hydroxymethane diphosphonic acid, (b) tetrasodium octyl hydroxymethane diphosphonic acid, (c) methane triphosphonic acid, (d) hexasodium methane triphosphonate, (e) methane tetraphosphonic acid, (f) octapotassium methane tetraphosphonate, (g) chloromethane triphosphonic acid, (h) disodium dichloromethane diphosphonate, (i) phenyl hydroxymethane diphosphonic acid, (j) tetrasodium phenyl hydroxymethane diphosphonate, and (k) phenyl methane diphosphonic acid.

Example 12

Octyl hydroxymethane diphosphonic acid, decyl hydroxymethane diphosphonic acid and their tetrasodium salts each reduced the surface tension of water from 70 dynes/cm. to less than 30 dynes/cm. when used at a concentration of 0.5%.

Example 13

A detergency test with 0.10% Ultrawet K and increasing amounts of methyl hydroxymethane diphosphonic acid at pH 9.5 in water showed that methyl hydroxymethane diphosphonic acid was superior to phytic acid and sodium tripolyphosphate at every concentration tested, namely, from 0.05% to 0.30%. This superiority was also noted for methane triphosphonic acid, methane tetraphosphonic acid and chloromethane triphosphonic acid when used in the same conditions.

Example 14

A solution of 0.002% of methyl hydroxymethane diphosphonic acid in a 0.05% aqueous solution of sodium metasilicate at a temperature of 90° protected the surface of aluminum immersed in it for at least 20 hours, while a control solution of the same sodium metasilicate caused extensive corrosion under the same conditions. Similarly, white metal, German silver, stainless steel and red brass were protected. In place of the methyl hydroxymethane diphosphonic acid there was also employed successfully the same amount of methane triphosphonic acid, methane tetraphosphonic acid, chloromethane triphosphonic acid and phenyl hydroxymethane diphosphonic acid.

Example 15

"Fab" is a commencial detergent comprising Alfol 14–18 (a mixture of 14–18 carbon atom alkyl alcohols), LAS (linear alkane sulfonates containing 10–18 carbon atoms), KXS (potassium xylene sulfonate and TKPP (tetrapotassium pyrophosphate). To improve the detergency power of "Fab" there was added 10% of methyl hydroxymethane diphosphonic acid.

The detergency power of "Fab" was also improved by adding 10% of each of the following materials (a) tetrasodium methyl hydroxymethane diphosphonate, (b) trisodium methyl hydroxymethane diphosphonate, (c) trisodium phenyl hydroxymethane diphosphonate, (d) tetrasodium phenyl hydroxymethane diphosphonate, (e) octasodium methane tetraphosphonate, (f) hexapotassium methane triphosphonate, (g) tetrasodium chloromethane diphosphonate, (h) tetrosodium decyl hydroxymethane diphosphonate or (i) disodium octadecenyl hydroxymethane diphosphonate.

Example 16

	Parts
Sodium dodecylbenzene sulfonate	30
Sodium tripolyphosphate	25
Sodium sulfate	14
Sodium silicate	5
Tetrasodium methyl hydroxymethane diphosphonate	25

This mixture can be dissolved in water to give a 0.2% detergent solution.

In place of the diphosphonate in Example 16 there can be used an equivalent amount of (a) octasodium methane tetraphosphonate, (b) tetrasodium methane tetraphosphonate, (c) hexasodium methane triphosphonate, (d) hexapotassium chloromethane triphosphonate, (e) tertasodium trichloromethyl hydroxymethane diphosphonate, (f) tetrapotassium heptadecyl hydroxymethane diphosphonate, (g) tetrasodium phenyl hydroxymethane diphos-

phonte, or (h) tetrasodium ethyl hydroxymethane diphosphonate.

Example 17

	Parts
Sodium tridecyl benzene sulfonate	30
Octasodium methane tetraphosphonate	50

This mixture can be dissolved in water to give a 0.2% detergent solution. In place of the tetraphosphonate there can be used an equal amount of (a) tetrasodium methyl hydroxymethane diphosphonate, (b) trisodium methyl hydroxymethane diphosphonate, (c) hexasodium methane triphosphonate, (d) tetrasodium dichloromethane diphosphonate, (e) pentasodium phenyl methane triphosphonate, (f) tetrasodium phenyl hydroxymethane diphosphonate, (g) tetrasodium chloromethyl hydroxymethane diphosphonate.

Example 18

	Parts
Sodium stearate	60
Soda ash	15
Tetrasodium pyrophosphate	5
Methane tetraphosphonic acid	10

This mixture also was a good detergent at 0.2% concentration. Soil redeposition properties of the composition were enhanced by adding 5 parts of polyvinyl alcohol and 5 parts of carboxymethyl cellulose. In place of the methane tetraphosphonic acid in Example 18 there can be used an equal amount of (a) octasodium methane tetraphosphonate, (b) methane triphosphonic acid, (c) hexasodium methane triphosphonate, (d) tetrasodium methyl hydroxymethane diphosphonate, (e) tetrasodium phenyl hydroxymethane diphosphonate, or (f) tetrasodium isononyl hydroxymethane diphosphonate.

Example 19

	Parts
Sodium hexadecane sulfonate	15
Sodium tripolyphosphate	5
Tetrasodium methyl hydroxymethane diphosphonate	5
Soda ash	5

Example 20

	Parts
Sodium tridecyl benzene sulfonate	40
Sodium tripolyphosphate	15
Trisodium phenyl hydroxymethane diphosphonate	20
Sodium silicate	10
Sodium sulfate	15
Sodium carboxymethyl cellulose	0.3
Polyvinyl alcohol (viscosity 2.34 centipoises, 22.3% polyvinyl acetate)	0.3

Example 21

	Parts
Sodium tridecyl benzene sulfonate	17
Cocoanut monoethanolamide	3
Sodium tripolyphosphate	15
Hexasodium methane triphosphonate	30
Sodium toluene sulfonate	2.4
Sodium silicate	5.5
Sodium sulfate	18

Example 22

	Parts
Nonylphenol-ethylene oxide adduct (9.5 ethylene oxide units)	12
Sodium tridecyl benzene sulfonate	1.75
Sodium tripolyphosphate	20
Hexasodium chloromethane triphosphonate	20
Sodium sulfate	35
Fluorescent dye	0.2

The sodium tridecyl benzene sulfonate had an alkyl group derived from a mixture of propylene tetramer and pentamer and averaged to a tridecyl group.

In place of the triphosphonate there can be used in this example the same amount of (a) tetrasodium propyl hydroxymethane diphosphonate, (b) octasodium methane tetraphosphonate, (c) tetrasodium decyl hydroxymethane diphosphonate, or (d) tetrasodium trichloromethyl diphosphonate.

Example 23

	Parts
Sodium tridecyl benzene sulfonate	8
Nonylphenol-ethylene oxide adduct	6
Sodium tripolyphosphates	15
Tetrasodium methane triphosphonate	20
Cetyl alcohol	0.8
Sodium silicate	3.0
Sodium sulfate	37.8
Sodium carboxymethyl cellulose	0.3
Polyvinyl alcohol	0.13

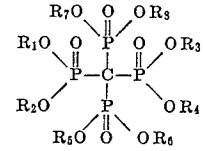
Example 24

	Parts
Sodium hardened tallow alcohol sulfate	10
Pentasodium tripolyphosphate	15
Tetrasodium ethyl hydroxymethane diphosphonate	20
Sodium silicate	10
Sodium carbonate	15
Sodium carboxymethyl hydroxyethyl cellulose	0.5
Sodium sulfate	19.45

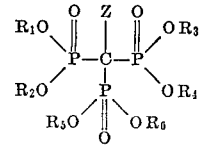
What is claimed is:

1. A detergent composition consisting essentially of a water soluble, synthetic detergent and a phosphorus compound having a formula selected from the group consisting of

(a)



(b)



where R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are selected from the group consisting of hydrogen, alkali metal and ammonium, and Z is selected from the group consisting of hydrogen, phenyl chlorine and bromine.

2. A composition according to claim 1 where the detergent is an anionic detergent.

3. A composition according to claim 1 wherein the detergent is an anionic detergent selected from the group consisting of sulfate and sulfonate detergents and soap.

4. A composition according to claim 3 wherein the phosphorus compound is a member of the group consisting of methane tetraphosphonic acid and its alkali metal salts.

5. A composition according to claim 3 wherein the phosphorus compound is a member of the group consisting of phenyl methane triphosphonic acid and its alkali metal salts.

6. A composition according to claim 3 wherein the phosphorus compound is a member of the group consisting of chloromethane triphosphonic acid and alkali metal salts of such acid.

7. A composition according to claim 3 including an alkali metal polyphosphate builder.

8. A composition according to claim 1 including a nonionic detergent.

9. A composition according to claim 1 including an alkali metal polyphosphate builder.

10. A composition according to claim 9 wherein the phosphorus compound is a member of the group consisting of methane tetraphosphonic acid and its alkali metal salts.

11. A composition according to claim 9 wherein the phosphorus compound is a member of the group consisting of phenyl methane triphosphonic acid and its alkali metal salts.

12. A composition according to claim 1 consisting essentially of the detergent, phosphorus compound and at least one member of the group consisting of alkali metal phosphate builders, silicates and alkali metal borates.

13. A composition according to claim 9 wherein the phosphorus compound is a member of the group consisting of chloromethane triphosphonic acid and its alkali metal salts.

14. A composition according to claim 9 wherein the phosphorus compound is a member of the group consisting of methane triphosphonic acid and its alkali metal salts.

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