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DETERGENT COMPOSITION

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U.S. Cl. 252—161 **5 Claims**
Int. Cl. C11d *1/37;* **C07f** *9/02;* **C11d** *1/10;* **C11d** *1/34*

This invention relates to a novel class of compounds and to improved detergent compositions containing such compounds. More particularly, this invention relates to a novel class of substituted methylene diphosphonic acid compounds and their water soluble salts which possess excellent detergency builder properties with a broad range of detergent surface active compounds. Novel laundering compositions whose cleaning powers are enhanced by these novel compounds are also described.

The use of builders as adjuncts to soap and synthetic detergents, and the property which some materials have of improving detergency levels of such detergent compounds is well known. The exact behavior and mechanics of how builders perform their function has never been fully explained, however. While many explanations for the behavior of builders may be found, there still has not been determined a set of criteria which would permit one to accurately predict which compounds actually possess builder properties.

This may be explained, in part, by the complex nature of detergency itself and the countless factors which are conceptually involved. Among the many facets of built detergency systems in which builder materials are thought to have some effect are such factors as stabilization of solid soil suspensions, emulsification of soil particles, the surface activity of the aqueous detergent solution, solubilization of water insoluble materials, foaming or suds producing characteristics of the washing solutions, peptization of soil agglomerates, neutralization of acid soil and inactivation of the mineral constituents present in the washing solution tending to "harden" it. Other areas could be mentioned in which a builder material might perhaps play an important role. The point is that no unequivocal rule has been found either as regards physical properties or chemical structures by which one might predict the behavior of chemical materials as detergent builders.

Among the builder materials described in the prior art, are water soluble inorganic alkaline builder salts which are used alone or in combination. Examples are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates.

Examples of organic builder compounds known heretofore and which also can be used alone and in combination are alkali metal, ammonium or substituted ammonium aminopolycarboxylates, e.g. sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylenediaminetriacetate, sodium and potassium nitrilotriacetate and sodium, potassium and triethanolammonium-N-(2-hydroxyethyl) - nitrilodiacetate. Alkali metal salts of phytic acid, e.g. sodium phytate are also suitable as organic builders.

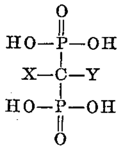
An ever increasing interest in builder materials as just described has resulted in the development of many candidates as builder materials. This increased interest has focused attention upon the need for improved builders which are free of the limitations and disadvantages inherent in prior art builder materials.

One such disadvantage is associated with probably the most widely used class of builder materials. This would be the series of condensed inorganic polyphosphate compounds such as alkali metal tripolyphosphates and higher condensed phosphates. These compounds have a strong tendency to hydrolyze when used in detergent compounds into less condensed phosphorus compounds which are relatively inferior builders and, in fact, form undesirable precipitates in the aqueous washing solution. An example of such a lower form is orthophosphate.

It is, therefore, a primary object of this invention to provide a novel class of compounds. Another object is to provide a novel class of substituted methylenediphosphonic acid compounds and their salts. Another object of this invention is to provide a novel class of compounds which are useful detergent builder compounds. Yet another object is to provide improved detergent compositions containing as the builder material a water soluble substituted methylenediphosphonate salt of the general structure described below. A yet further object is to provide improved built detergent compositions in which the builder material is a substituted methylenediphosphonate water soluble salts of this invention which built compositions are surprisingly effective in cool water washing situations. Another object is to provide detergent compositions in which the builder compound is one specified below and the detergent active is selected from a broad class of detergent surfactant materials.

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 from this detailed description to those skilled in the art.

According to this invention the new class of substituted methylenediphosphonic acid compounds has the following general formula:



$$\begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{HO-P-OH} \\ | \\ \mathrm{X-C-Y} \\ | \\ \mathrm{HO-P-OH} \\ \| \\ \mathrm{O} \end{array}$$

wherein X and Y are each selected from the group consisting of a methyl radical, a benzyl radical, halogen, carboxymethylene radical, and hydrogen, at least one of X and Y being other than hydrogen.

Compounds conforming to the above formula constitute a previously unknown class of compounds. The members of this class have many uses. For instance, they can serve as valuable intermediates in the production of other compounds such as phosphine oxide derivatives which are known surface active materials. Moreover, phosphine oxides made from the compounds of this invention can be used as recovery agents for uranium.

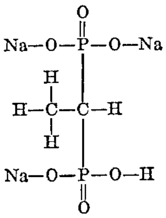
More especially, however, water soluble derivatives of the new compounds of this invention surprisingly have been discovered to be highly efficient detergency builders. They offer as an advantage over previously known builder compounds the possibility of using proportionally smaller amounts of builder compound without sacrificing in overall cleaning performance. Other similarly valuable advantages are discussed hereinafter.

While any alkali metal or ammonium or substituted ammonium (e.g. triethanol ammonium) salt form can be prepared according to this invention, the alkali metal derivatives are the preferred forms. Suitable alkali metals include sodium and potassium. The compounds herein are generally obtained as the tetrasodium and trisodium salts as prepared according to this invention. Each of the lesser neutralized forms such as monosodium and disodium derivatives or the free acid form have comparable builder capacity to the trisodium and tetrasodium salt forms, provided, that additional alkali is added to adjust the pH of the washing solution to be within a range of from about 8 to about 12. The standard alkaline materials can be used for this purpose, such as alkali metal silicates, phosphates, borates and carbonates. Free alkali materials such as sodium and potassium hydroxides can be used also.

Specific illustrations of the newly discovered compounds include the following alkali metal derivatives. The trisodium salt is exemplified but, of course, other alkali metal and water soluble salts are within the scope of this invention.

(1) trisodium ethylidenediphosphonate,

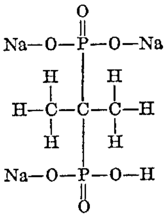
$CH_3CH(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{ccccc} & & O & & \\ & & \| & & \\ Na-O- & & P & -O-Na & \\ & H & | & & \\ & | & | & & \\ H- & C & -C & -H & \\ & | & | & & \\ & H & | & & \\ Na-O- & & P & -O-H & \\ & & \| & & \\ & & O & & \end{array}$$

(2) trisodium isopropylidenediphosphonate,

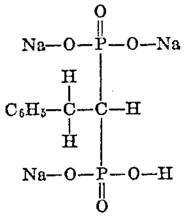
$(CH_3)_2C(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{ccccc} & & O & & \\ & & \| & & \\ Na-O- & & P & -O-Na & \\ & H & | & H & \\ H- & C & -C- & C & -H \\ & H & | & H & \\ Na-O- & & P & -O-H & \\ & & \| & & \\ & & O & & \end{array}$$

(3) trisodium benzyl-methylenediphosphonate,

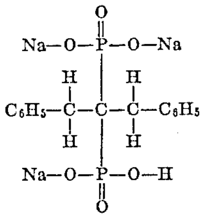
$C_6H_5CH_2(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{ccccc} & & O & & \\ & & \| & & \\ Na-O- & & P & -O-Na & \\ & H & | & & \\ C_6H_5- & C & -C & -H & \\ & H & | & & \\ Na-O- & & P & -O-H & \\ & & \| & & \\ & & O & & \end{array}$$

(4) trisodium bis(benzyl)-methylenediphosphonate

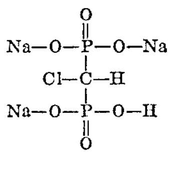
$(C_6H_5CH_2)_2C(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{ccccc} & & O & & \\ & & \| & & \\ Na-O- & & P & -O-Na & \\ & H & | & H & \\ C_6H_5- & C & -C- & C & -C_6H_5 \\ & H & | & H & \\ Na-O- & & P & -O-H & \\ & & \| & & \\ & & O & & \end{array}$$

(5) trisodium monochloromethylenediphosphonate,

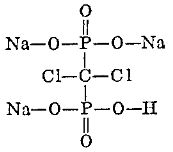
$ClCH(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{c} O \\ \| \\ Na-O-P-O-Na \\ | \\ Cl-C-H \\ | \\ Na-O-P-O-H \\ \| \\ O \end{array}$$

(6) trisodium dichloromethylenediphosphonate,

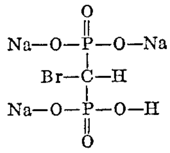
$Cl_2C(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{c} O \\ \| \\ Na-O-P-O-Na \\ | \\ Cl-C-Cl \\ | \\ Na-O-P-O-H \\ \| \\ O \end{array}$$

(7) trisodium monobromomethylenediphosphonate,

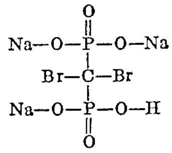
$BrCH(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{c} O \\ \| \\ Na-O-P-O-Na \\ | \\ Br-C-H \\ | \\ Na-O-P-O-H \\ \| \\ O \end{array}$$

(8) trisodium dibromomethylenediphosphonate,

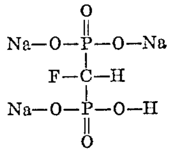
$Br_2C(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{c} O \\ \| \\ Na-O-P-O-Na \\ | \\ Br-C-Br \\ | \\ Na-O-P-O-H \\ \| \\ O \end{array}$$

(9) trisodium monofluoromethylenediphosphonate,

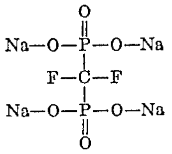
$FCH(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{c} O \\ \| \\ Na-O-P-O-Na \\ | \\ F-C-H \\ | \\ Na-O-P-O-H \\ \| \\ O \end{array}$$

(10) trisodium difluoromethylenediphosphonate,

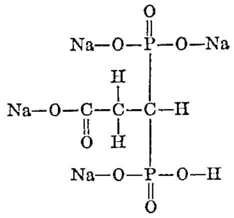
$F_2C(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{c} O \\ \| \\ Na-O-P-O-Na \\ | \\ F-C-F \\ | \\ Na-O-P-O-Na \\ \| \\ O \end{array}$$

(11) tetrasodium-2-carboxyethylidenediphosphonate,

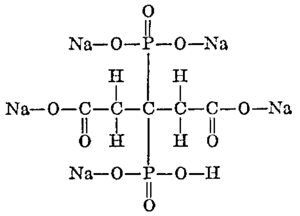
$NaO_2CCH_2CH(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{cccccc} & & & O & & \\ & & & \| & & \\ & Na-O- & & P & -O-Na & \\ & & H & | & & \\ Na-O- & C- & C & -C & -H & \\ & \| & | & | & & \\ & O & H & | & & \\ & Na-O- & & P & -O-H & \\ & & & \| & & \\ & & & O & & \end{array}$$

(12) pentasodium-bis(carboxymethyl)methylenediphosphonate

$(NaO_2CCH_2)_2C(PO_3Na_2)(PO_3NaH)$



$$\begin{array}{ccccccc} & & & O & & & \\ & & & \| & & & \\ & & Na-O- & P & -O-Na & & \\ & & H & | & H & & \\ Na-O- & C- & C- & C & -C & -C & -O-Na \\ & \| & | & | & | & \| & \\ & O & H & | & H & O & \\ & & Na-O- & P & -O-H & & \\ & & & \| & & & \\ & & & O & & & \end{array}$$

Synthesis routes of these novel compounds essentially involve, as a first step, an oxidation-reduction type of a reaction between a metallating agent such as sodium, sodium hydride, potassium or potassium-sodium eutectic alloy, and a tetraalkyl ester of methylenediphosphonic acid. This reaction is highly exothermic and it is essential that it be conducted at low temperatures on the order of 0° C. to 35° C., and preferably between 15° C. and 30° C. The reaction product is a carbanion derived from the active methylene grouping present in the parent methylene ester starting material. The equation for this step is as follows:

$$Na+H_2C[PO(OR)_2]_2 \rightarrow \tfrac{1}{2}H_2+[PO(OR_2)_2HC^-Na^+]$$

This carbanion reaction product is then reacted with a suitable alkylating agent or halogenating agent in order to obtain the desired substituted methylenediphosphonate tetraalkyl ester.

The phosphonate esters so derived can usually be purified by simple distiilative means, if desired, after removal of by-product salts. More often, the crude product is converted directly to the free phosphonic acid by methods kwnown to those skilled in the art, namely, by hydrolyzing with concentrated hydrochloric acid or in the case of isopropyl esters, by pyrolysis. An excellent novel pyrolytic process is described in a copending application Ser. No. 218,863, filed Aug. 23, 1962, by Clarence H. Roy. Addition of base such as sodium hydroxide and potassium hydroxide to the acids results in formation of the corresponding salts.

The tetraalkyl ester of methylene diphosphonic acid used as a starting material for preparing the novel compounds of this invention can be prepared according to the following method.

Preparation of tetraisopropyl methylenediphosphonate

624.7 gm. of triisopropyl phosphite (3 moles, 681 ml.) and 173.9 gm. of dibromoethane (1 mole, 70 ml.) were combined in a reaction apparatus composed of a 1-liter, 3-neck flask fitted with a magnetic stirrer, a thermometer, and a fractionating column for separating the isopropyl bromide by-product from the refluxing mixture. The fractionating column was constructed from a 36-inch Liebig condenser that had been modified to accommodate ¼-inch glass helices as packing. A Barrett distilling receiver, which had been modified by the addition of a thermometer well and thermometer was connected to the top of the fractionating column; and to the top of the Barrett receiver was fitted a Dewar condenser cooled with Dry Ice and protected from atmospheric moisture by a drying tube. The temperature of the reaction mixture was quickly brought to reflux at 143° C. The temperature of the circulating water in the packed reflux condenser was maintained at 65° C. This temperature was sufficient to return unreacted starting material and allow the by-product isopropyl bromide to be distilled. The heat input to the reaction was such that vigorous refluxing continued as the temperature of the mixture slowly increased. After about two hours of heating the first distillate was observed, and after five hours a total of 33 gm. of isopropyl bromide had been collected. The temperature of the reaction mixture was allowed to increase to 185° C. over a twelve hour period, and by means of an electronic temperature controller it was held there for the remainder of the reaction.

After approximately 16 hours, the reaction was essentially complete as judged by the yield of isopropyl bromide, 231 gm. which represented a yield of about 92%. Further heating served no useful purpose, although reaction times of 20 hours were employed on occasion.

When the reaction was completed, the reaction mixture was transferred to a distilling flask and the low boiling materials (excess phosphite, etc.) were removed through a short one-piece still under a vacuum of 0.1 mm. of mercury and head temperatures up to 50° C. At this point the contents of the flask weighed approximately 330 gm. and was 93% to 95% tetraisopropyl methylenediphosphonate. The purity of this material was sufficient to proceed in the synthesis of the novel compounds of this invention.

If a purer product is desired, a high capacity vacuum pump can be introduced into the system and the pressure reduced to 0.005 mm. of mercury. The material boiling between 80° C. and 116° C. is collected and redistilled through an electrically heated 24-inch Vigreaux column. A complete example of this type of process is presented in a copending patent application, Ser. No. 218,862, filed Aug. 23, 1962, by Clarence H. Roy.

In the preparation of the tetraalkyl ester reactant, particular care must be taken to insure that the starting materials are pure and freshly distilled because the presence of acidic residues in the product causes premature decomposition upon attempted distillation. If this occurs, the product must be neutralized at once, whereupon distillation may be resumed. The neutralization is time consuming and laborious, and is not recommended as an alternative to initial purification of reactants.

It should be noted that a product obtained by fractionation through a Vigreaux column is very nearly as pure as that obtained by careful fractionation through a 24-inch spinning band column; also the yield is much improved because the faster throughput reduces heating time and consequently, reduces the amount of undistillable resinous residues. The resinous residue in the flask should not be discarded, however, because hydrolysis of this material will yield methylenediphosphonic acid of remarkable purity.

The tetraalkyl methylenediphosphonate compound prepared according to the process just described or the process described in the copending application noted above can be used in this invention as illustrated in the following example.

EXAMPLE I

(A) Preparation of tetraisopropyl ethylidenediphosphonate

Sodium, 11.5 gm. (0.5 mole) was dispersed in 200 ml. of boiling toluene contained in a 500 ml., three-neck flask which was fitted with a dropping funnel, a Friedrich's condenser, and a high speed stirrer. The sodium dispersion was cooled to 20° C. and 172.2 gm. (0.5 mole, 181.2 ml.) of tetraisopropyl methylenediphosphonate was added dropwise at a rate such that the reaction could be controlled and a temperature of less than 30° C. maintained by external cooling with Dry Ice. When this reaction was complete the high speed stirrer was replaced by a magnetic stirrer. Iodomethane (0.55 mole, 78 gm.) was added dropwise to the stirred solution while the temperature was held below 30° C. This reaction was very exothermic and required considerable cooling. When the addition was completed, the reaction mixture was a clear yellow, homogeneous solution, and heat was cautiously applied. The temperature was gradually raised to 80° C. and held there for 3.5 hours. The sodium iodide which had precipitated was filtered and the filtrate was reduced to a constant volume in vacuo. The viscous, oily, residue was diluted with 350 ml. of water and extracted with hexane for fifteen hours in a continuous extractor. When the hexane solution was reduced to a constant volume, 154 gm. of crude tetraisopropyl ethylidenediphosphonate remained constituting a yield of 84.9%, N_D^{25} 1.4319.

Analysis.—Calculated for $C_{14}H_{32}O_6P_2$: C, 46.92; H, 9.00; P, 17.29. Found: C, 46.27; H, 9.14; P, 16.66.

(B) Conversion to ethylidenediphosphonic acid

A 3.73 gm. sample of pure tetraisopropyl ethylidenediphosphonate was refluxed for three hours in 50 ml. of concentrated hydrochloric acid. The acidic solution was reduced to a constant volume in a flash evaporator, and the viscous residue was azeotropically dried by evaporation with three portions of isopropyl alcohol. The residue was subjected to a vacuum of 0.07 mm. of mercury until small crystals appeared (about three hours). After standing overnight, the crystalline product was filtered with the aid of isopropyl alcohol and acetone washes. When dry, the yield of ethylidenediphosphonic acid was 0.89 gm., 45.2% M.P. 179°–181° C.

Analysis.—Calculated for $C_2H_8P_2O_6$: C, 12.64; H, 4.24; P, 32.60. Found: C, 12.64; H, 4.20; P, 32.15.

EXAMPLE II

Trisodium ethylidenediphosphonate

A practical preparation of the title salt was accomplished by refluxing 154 gm. of crude tetraisopropyl ethylidenediphosphonate prepared according to Example I(A) in 500 ml. of concentrated hydrochloric acid for five hours. The reaction mixture was concentrated to a constant volume and seeded with a few crystals of acid from a previous preparation. The seeded viscous product was then rotated in a flash evaporator under high vacuum until the entire mass had crystallized. The crystalline product was removed from the flask with acetone washes, and an almost theoretical yield of crude ethylidenediphosphonic acid product (M.P. 159°–163° C.) was obtained. Addition of three equivalents of sodium hydroxide to an aqueous solution of this acid resulted in formation of the trisodium salt which could be used directly in a laundering composition.

EXAMPLE III

(A) Preparation of tetraisopropyl isopropylidenediphosphonate

A sodium dispersion was prepared by dispersing 22.99 gm. (1 mole) of sodium in 200 ml. of boiling toluene contained in a one liter, three-neck flask which was fitted with a thermometer, a 50 ml. offset, additive-type separatory funnel, an Allihn condenser, and a high speed stirrer. After cooling the dispersion to 20° C. tetraisopropyl ethylidenediphosphonate,

$$CH_3CH[PO(OC_3H_7\text{-i})_2]_2$$

(358.36 gm., 1 mole) was added dropwise to the dispersion. The exothermic reaction was controlled and a temperature of 25°–30° C. was maintained by external cooling with a Dry Ice bath. Reaction was complete after 30 minutes, and dry methyl bromide was bled into the reaction mixture via a sintered glass diffusion tube.

Again, the temperature was kept at less than 30° C. during the evolution of heat, which lasted 30 minutes. An excess of methyl bromide was added and the mixture heated to 60° C. for one hour. The solvent and excess methyl bromide were removed by evaporation under vacuum. The remaining mixture was dissolved in 700 ml. of hexane and extracted with water until the water extract was halide free. The hexane solution was dried with $MgSO_4$ and concentrated in vacuo to give 368 gm. of crude tetraisopropyl isopropylidenediphosphonate,

$$(CH_3)_2C[PO(OC_3H_7\text{-i})_2]_2$$

N_D^{25} 1.4322, yield 98.4%.

Analysis.—Calculated for $C_{14}H_{34}O_6P_2$: C, 48.38; H, 9.20; P, 16.64. Found: C, 47.9; H, 9.40; P, 15.4.

This same compound can be prepared by starting with tetraisopropyl methylidenediphosphonate,

$$CH_2[PO(OC_3H_7\text{-i})_2]_2$$

reacting with a double molar amount of sodium and then with two equivalents of methyl bromide. However, under the conditions employed for the preceding reaction, a mixture of $(CH_3)_2C[PO(OC_3H_7\text{-i})_2]_2$;

$$CH_3CH[PO(OC_3H_7\text{-i})_2]_2$$

$CH_2[PO(OC_3H_7\text{-i})_2]_2$ was obtained.

(B) Conversion to isopropylidenediphosphonic acid

An 18 gram (.48 mole) sample of analytically pure tetraisopropyl isopropylidenediphosphonate,

$$(CH_3)_2C[PO(OC_3H_7\text{-i})_2]_2$$

was dissolved in 150 ml. of concentrated hydrochloric acid and refluxed for four hours. The solution was concentrated to a constant volume with a flash evaporator and traces of water removed by twice azeotroping with 2-propanol. The crystalline material remaining was filtered and washed with a 1:1 mixture of acetone-ether, yielding 9.3 grams of isopropylidenediphosphonic acid,

$$(CH_3)_2C[PO(OH)_2]_2$$

M.P. 228.5° C.–229.5° C., yield 95.5%.

Analysis.—Calculated for $C_3H_{10}O_6P_2$: C, 17.66; H, 4.94; P, 30.36. Found: C, 17.7; H, 5.0; P, 28.9.

EXAMPLE IV

(A) Preparation of tetraisopropyl benzyl-methylenediphosphonate

Sodium, 16.09 gm. (0.7 mole) was disposed in 150 ml. of boiling toluene contained in a one liter, three-neck flask which was fitted with a thermometer, a 50 ml. offset, additive type separatory funnel, an Allihn condenser, and a high speed stirrer. The dispersion was cooled to 20° C. and 241.8 gm. (0.7 mole) tetraisopropyl methylenediphosphonate, of $CH_2[PO(OC_3H_7\text{-i})_2]_2$ was added dropwise at a rate such that the reaction temperature could be controlled and maintained at 25° C.–30° C. by external cooling with a Dry-Ice bath. When this reaction had reached completion, the reaction mixture was heated to 100° C. and benzyl bromide (0.7 mole, 120 gm.) was added dropwise to the stirred solution. The heat evolved by the reaction was sufficient to maintain the temperature of 100° C. for 20 minutes, after which the temperature began slowly dropping. A heating mantle was applied to the reaction flask and the temperature kept at 60° C. for one hour. The reaction mixture was then concentrated to a constant volume in vacuo; and the remaining material dissolved in 700 ml. of hexane and extracted with water until halide free. Reduction of the hexane solution to constant in vacuo volume gave 260 gm. of crude tetraisopropyl benzyl-methylenediphosphonate,

$$C_6H_5CH_2CH[PO(OC_3H_7\text{-i})_2]_2$$

yield 85.5%, N_D^{25} 1.4742.

Analysis.—Calculated for $C_{20}H_{36}O_6P_2$: C, 55.29; H, 8.35; P, 15.26. Found: C, 56.48; H, 8.34; P, 14.41.

(B) Conversion to benzyl-methylenediphosphonic acid

A 72.6 gram (0.167 mole) sample of pure tetraisopropyl benzyl-methylenediphosphonate,

$$C_6H_5CH_2[PO(OC_3H_7\text{-i})_2]_2$$

was dissolved in 500 ml. of concentrated hydrochloric acid and refluxed for four hours. The reaction mixture was reduced to a constant volume on a flash evaporator and the last traces of water and HCl were removed by adding three portions of 2-propanol and reducing the volume after each addition. The crystalline mass which remained in the evaporating flask was filtered and washed with acetone, and dried in a vacuum desiccator over a mixture of silica gel and potassium hydroxide, leaving 43.7 gm. of benzyl-methylenediphosphonic acid,

$$C_6H_5CH_2CH[PO(OH)_2]_2$$

M.P. 210° C.–212° C., yield 98.2%.

Analysis.—Calculated for $C_8H_{12}O_6P_2$: C, 36.11, H, 4.55, P, 23.28. Found: C, 36.20; H, 4.66; P, 23.5.

EXAMPLE V

(A) Preparation of tetraisopropyl bromomethylenediphosphonate

A 0.5 mole sample of tetraisopropyl methylenediphosphonate carbanion (sodium salt) was prepared in the same manner and using similar reaction apparatus as in the foregoing examples. Bromine (79.92, 0.5 mole) was added dropwise to the reaction mixture employing the Dry Ice bath as before to maintain a temperature of less than 30° C. Following the completion of the reaction, the mixture was concentrated to a constant volume, dissolved in 600 ml. of hexane and extracted with water until the extract was halide free. Concentration of the hexane solution gave 200 grams of product which was predominantly tetraisopropyl bromomethylenediphosphonate, $BrCH[PO(OC_3H_7\text{-}i)_2]_2$; yield 95.4%. Although purification of this material by distillation was somewhat difficult, repeated refractionation rectified the mixture, giving a pure product, N_D^{25} 1.4594.

Analysis.—Calculated for $BrC_{13}H_{29}O_6P_2$; Br, 18.81; C, 36.89; H, 6.91; P, 14.64. Found: Br, 18.10; C, 37.18; H, 7.15; P, 15.00.

(B) Conversion to bromomethylenediphosphonic acid

A 37.1 gram (0.09 mole) sample of tetraisopropyl bromomethylenediphosphonate $BrCH[PO(OC_3H_7\text{-}i)_2]_2$, contaminated with a small percentage of tetraisopropyl dibromomethylenediphosphate, $Br_2C[PO(OC_3H_7\text{-}i)_2]_2$, was dissolved in 250 ml. of concentrated hydrochloric acid and refluxed for five hours. After concentration of the acid solution and azeotroping with 2-propanol to remove traces of water, various attempts to crystallize the viscous product (22 gm. 98.5% yield) were unsuccessful. In order to obtain an analytical sample, excess aniline was added to convert the acid to the dianilinium salt. The salt was purified by recrystallization from a water-methanol mixture. The pure dianilinium salt thus obtained melted at 185°–187° C.

Analysis.—Calculated for $BrC_{13}H_{19}O_6P_2N_2$: Br, 18.1; C, 35.39; H, 4.34; P, 14.1; N, 6.35; Found: Br, 18.8; C, 35.0; H, 4.3; P, 14.8; N, 5.25.

EXAMPLE VI

(A) Preparation of tetraisopropyl dichloromethylenediphosphonate

The carbanion of 1 mole (344.3 gm.) of tetraisopropyl methylenediphosphonate, $CH_2[PO(OC_3H_7\text{-}i)_2]_2$, was prepared by reacting equal molar amounts of tetraisopropyl methylenediphosphonate with sodium using the same general procedure and reaction apparatus as in the foregoing examples. Dry chlorine was bled into the reaction mixture which was kept at 20° C.–30° C. throughout the exothermic reaction by external cooling with a Dry Ice bath. Heat evolution ceased after 45 minutes of reaction, a 100% excess of chlorine being consumed during this time. The reaction mixture was heated to 70° C. for one hour and then was stirred for two days at room temperature. The resulting mixture was concentrated to a constant volume, dissolved in 800 ml. of hexane and extracted with water until the extract was halide free. The hexane solution was dried with $MgSO_4$ and concentrated to yield 399 grams of crude tetraisopropyl dichloromethylenediphosphonate, $Cl_2C[PO(OC_3H_7\text{-}i)_2]_2$, a 94.5% yield. This material slowly crystallized, giving a product melting at 49.8° C.–51° C. A density of 1.543 at 25° C. and a refractive index of 1.4518 also at 25° C. were obtained before the product solidified.

Analysis.—Calculated for $Cl_2C_{13}H_{28}O_6P_2$: Cl, 17.16; C, 37.79; H, 6.83; P, 14.99. Found: Cl, 17.42; C, 37.89; H, 6.71; P, 14.6.

(B) Conversion to dichloromethylenediphosphonic acid

A 41.3 gram (0.1 mole) of pure tetraisopropyl dichloromethylenediphosphonate, $Cl_2C[PO(OC_3H_7\text{-}i)_2]_2$, was converted to dichloromethylenediphosphonic acid, $Cl_2C[PO(OH)_2]_2$, by refluxing with 250 ml. of concentrated hydrochloric acid. The acidic solution was concentrated to a constant volume and twice azeotroped with 2-propanol to remove the last traces of water and HCl. The resulting crystalline mass was filtered and washed with acetone, then dried in a vacuum desiccator over silica gel and potassium hydroxide. The 23.9 gm. (98% yield) of very hydroscopic acid thus obtained melted at 249° C.–251° C.

Analysis.—Calculated for $Cl_2CH_4O_6P_2$; Cl, 28.95; C, 4.91; H, 1.65; P, 25.30: Found: Cl, 28.63; C. 4.85; H, 1.80; P, 25.0.

Neutralization of the above acid with four equivalents of sodium hydroxide yielded the tetrasodium salt, which was isolated as the octahydrate.

Analysis.—Calculated (on a dry basis) for

$$Cl_2CO_6P_2Na_2$$

Cl, 21.3; C, 3.6; P, 18.6; Na, 27.6. Found: Cl, 21.3; C, 4.0; P, 18.3; Na, 27.8.

EXAMPLE VII

(A) Preparation of tetraisopropyl dibromomethylenediphosphonate

The dibrominated methylenediphosphonate was obtained from the repeated refractionations of the mixture of monobromo, $BrCH[PO(OC_3H_7\text{-}i)_2]_2$, and dibrominated products, $Br_2C[PO(OC_3H_7\text{-}i)_2]_2$, mentioned in Example V. The tetraisopropyl dibromomethylenediphosphonate, $Br_2C[PO(OC_3H_7\text{-}i)_2]_2$ had an N_D^{25} of 1.4710.

Analysis.—Calculated for $Br_2C_{13}H_{23}O_6P_2$: Br. 31.89; C, 31.16; H, 5.63; P, 12.36. Found: Br, 31.2; C, 31.5; H, 5.72; P, 12.0.

(B) Conversion to dibromomethylenediphosphonic acid

Dibromomethylenediphosphonic acid was recovered by repeated recrystallization of a mixture of the aniline salts of a monobrominated and dibrominated product with a water-methanol solvent system, as in Example V–B. The salt obtained melted at 270°–217° C.

Analysis.—Calculated for $Br_2C_{13}H_{18}O_6P_2N_2$: Br, 30.74; C, 30.0; H, 3.48; P, 11.9; N, 5.39. Found: Br, 29.5; C, 31.0; H, 3.8; P, 12.2; N, 5.4. Addition of two equivalents of sodium hydroxide to an aqueous solution of this salt resulted in formation of the disodium salt.

EXAMPLE VIII

(A) Preparation of tetraisopropyl 2-carbethoxyethylidenediphosphonate

A sodium dispersion was prepared by dispersing 22.99 grams (1 mole) of sodium in boiling toluene contained in a one liter, three neck flask fitted with a thermometer, a high speed stirrer, a 50 ml. offset additive type separatory funnel, and an Allihn condenser. A Dry Ice bath was employed to maintain the temperatures in the desired range during the reaction. After the dispersion was cooled to 25° C., 344.33 grams (1 mole) of tetraisopropyl methylenediphosphonate $CH_2[PO(OC_3H_7\text{-}i)_2]_2$, was added dropwise to the reaction vessel over a 45 minute period, keeping the reaction temperature at 20° C.–30° C. by partial immersion of the reaction flask in the Dry Ice bath. The reaction reached completion ten minutes after all of the starting ester had been added. One mole (122.55 gm.) of ethyl chloroacetate ($C_3H_5OCOCH_2Cl$) was then added dropwise to the solution over a 30 minute period, again controlling the exothermic reaction with the Dry Ice bath. Following addition of all the ethyl chloroacetate, the mixture was heated to 60° C. for one hour. The solvent was then removed under vacuum and the residue dissolved in 600 ml. of hexane and extracted with water until the water extract was halide free. The hexane solution was dried with anhydrous $MgSO_4$, concentrated, and then distilled to give 86 grams of the tetraisopropyl 2-carbethoxy-ethylidenediphosphonate, $C_2H_5OCOH_2CH[PO(OC_3H_7\text{-}i)_2]_2$, N_D^{25} 1.4388, yield 20%.

Analysis.—Calculated for $C_{17}H_{36}O_8P_2$: C, 47.4; H, 8.4; P, 14.4. Found: C, 47.2; H, 8.7; P, 14.0.

(B) Conversion to 2-carboxy-ethylidenediphosphonic acid

A 43 gram sample (0.1 mole) of tetraisopropyl 2-carbethoxyethylidenediphosphonate,

$$C_2H_5OCH_2CH[PO(OC_3H_7\text{-}i)_2]_2$$

was dissolved in 250 ml. of concentrated hydrochloric acid and refluxed for four hours. The resulting solution was then concentrated to a constant volume on a flash evaporator. Traces of water and HCl were removed by adding two 100 ml. portions of 2-propanol and concentrated after each addition. A total of 23.1 grams (98.4% yield) of colorless, glassy material which had the theoretically correct P^{31} and proton nuclear magnetic resonance spectra for 2-carboxy-ethylidenediphosphonic acid was obtained; but standing in a vacuum disiccator did not produce a crystalline product.

Analysis.—Calculated for $C_3H_8O_8P_2$: C, 15.4; H, 3.5; P, 26.5. Found: C, 15.8; H, 3.8; P, 26.3.

Each of the acids prepared above is very easily converted to a salt form by reacting with a base such as sodium hydroxide, as illustrated for instance in Example VI. The resulting compounds perform as excellent detergency builder materials as mentioned previously and also as exemplified hereinafter.

As mentioned above, it has already been suggested to combine synthetic detergent compounds with various builder salts to produce built detergent compositions. No one prior to this invention, however, has employed the particular combination of compounds and proportions described herein that offer as advantages stability against deterioration during storage and use, high detergent power, and outstanding performance in hard water, as well as excellent whiteness and whiteness maintenance results.

These and other advantages are obtained according to this invention by providing detergent compositions consisting essentially of an organic detergent surfactant compound and, as a builder, an organic water soluble salt of one of the new compounds identified above, the ratio by weight of the builder to the detergent surfactant compound being in the range of about 1:3 to about 10:1 said composition providing in solution a pH of between about 8 to about 12. The preferred ratio of builder to said detergent surfactant compound is in the range of about 1:2 to about 5:1 and the optimum pH range is between 9.5 to 11.5.

Among the organic detergent surfactant compounds which can be successfully built by compounds prepared according to this invention are anionic, nonionic, ampholytic and zwitterionic detergent surfactants, and mixtures thereof.

(a) The anionic organic detergents include both soap and non-soap detergents.

Examples of suitable soaps are the sodium, potassium, ammonium and alkylolammonium salts of higher fatty acids (C_{10}–C_{20}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

The non-soap anionic synthetic detergents can be broadly described as the water soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl are higher acyl radicals.) Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are the sodium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8–C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkylbenzenesulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, especially those of the types described in United States Letters Patent Nos. 2,220,099 and 2,477,383; sodium alkylglycerylethersulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkylphenol ethylene oxide ether sulfates with about 1 to 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 to about 12 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide, where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a methyltauride in which the fatty acids, for example, are derived from coconut oil, and others known in the prior art, a number being specifically set forth in United States Patent Nos. 2,486,921, 2,486,922, and 2,386,278.

(b) Nonionic synthetic detergents: This class of synthetic detergents may be broadly defined as compounds aliphatic or alkyl aromatic in nature which do not ionize in water solution.

For example, a well known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with an hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility has a molecular weight of from about 1200 to 2500. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(1) The polyethylene oxide condensates of alkylphenols, e.g. the condensation products of alkylphenols or dialkylphenols wherein the alkyl group contains from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, said ethylene oxide being present in amounts equal to 8 to 25 moles of ethylene oxide per mole of alkylphenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, n-octene, or n-nonene, for example.

(2) Those nonionic compounds derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylenediamine and excess propylene oxide, said base having a molecular weight on the order of 2,500 to 3,000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g. a coconut alcohol ethylene oxide condensation having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(4) Long chain tertiary amine oxides corresponding to the following general formula,

$$R_1R_2R_3N \rightarrow O$$

wherein R_1 is an alkyl radical of from about 8 to 18 carbon atoms, and R_2 and R_3 are each methyl or ethyl radicals. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethyldecylamine oxide, dimethyltetradecylamine oxide, dimethylhexadecylamine oxide.

(5) Long chain tertiary phosphine oxides corresponding to the following general formula

$$RR'R''P\rightarrow O$$

wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 18 carbon atoms in chain length and R′ and R″ are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphine oxides are:

dimethyldodecylphosphine oxide,
dimethyltetradecylphosphine oxide,
ethylmethyltetradecylphosphine oxide,
cetyldimethylphosphine oxide,
dimethylstearylphosphine oxide,
cetylethylpropylphosphine oxide,
diethyldodecylphosphine oxide,
diethyltetradecylphosphine oxide,
dipropyldodecylphosphine oxide,
bis-(hydroxymethyl)dodecylphosphine oxide,
bis-(2-hydroxyethyl)dodecylphosphine oxide,
(2-hydroxypropyl)methyltetradecylphosphine oxide,
dimethyloleylphosphine oxide, and
dimethyl-(2-hydroxydodecyl)phosphine oxide.

(c) Ampholytic synthetic detergents: This class of synthetic detergents can be broadly described as derivatives of aliphatic amines which contain a long chain of about 8 to 18 carbon atoms, and an anionic water solubilizing group, e.g. carboxy, sulfo, or sulfato. Examples of compounds falling within this definition are sodium-3-dodecylaminopropionate and sodium-3-dodecylaminopropanesulfonate.

(d) Zwitterionic synthetic detergents: This class of synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium compounds, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g. carboxy, sulfo, or sulfato. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate.

The anionic, nonionic, ampholytic and zwitterionic detergent surfactants mentioned above can be used singly or in combination in the practice of the present invention. The above lists of examples are not intended to be complete but merely specific illustrations of the numerous detergents which can find application within the scope of this invention.

The foregoing organic synthetic detergent compounds and the novel builder compounds of this invention can be formulated according to any of the several commercially desirable composition forms, for example, granular, flake, liquid and tablet form.

Granular detergent compositions according to one embodiment of this invention can contain a representative builder and the detergent active in the ratio of about 1:3 to about 10:1. The preferred ratio of builder to detergent active in a granular product is about 1:2 to about 5:1.

Another special embodiment of this invention is a liquid detergent composition also containing a builder and a detergent active in the ratio of about 1:3 to about 10:1. On the other hand, the preferred ratios and optimum detergency results with liquid compositions obtain when the builder and the detergent active are mixed in ratios by weight of about 1:2 to about 3:1, respectively. The potassium salt form of the builder compounds is preferred for use in built liquid compositions.

The detergent compositions employing the builder compounds of this invention have special and unusually outstanding applicability in the area of built liquid detergents. This area presents special problems to the formulator in view of the peculiarities inherent in aqueous systems and the special requirements of solubility of the ingredients and, more especially, their stability in such mediums. It is well known, for instance, that sodium tripolyphosphate, which is outstanding in its behavior in granular compositions, is generally regarded as being unsuited for built liquid detergents. It has a fairly strong propensity to hydrolyze into lower forms of phosphates. Thus, as a practical consideration there has been a necessity of resorting to a more stable form of phosphate such as alkali metal pyrophosphates, for example, $Na_4P_2O_7$ or $K_4P_2O_7$. It has thus been necessary sometimes to sacrifice the excellent builder properties of sodium tripolyphosphate in order to prepare a more stable built liquid detergent product.

In view of the increasing acceptance by the general public of built liquid detergents for virtually all washing and cleaning situations including laundering and dishwashing, it is a significant contribution of this invention that an improved built liquid detergent product is made possible that will provide detergency levels comparable to and in some aspects superior to a sodium tripolyphosphate or potassium pyrophosphate built liquid product without the troublesome problem of stability.

Most of the built liquid detergents commercially available at the present time are either water based or have a mixture of water and alcohol as the liquid vehicle. Such vehicles can be employed in formulating a built liquid detergent product according to this invention without fear of encountering stability problems. Accordingly, a sample built liquid detergent composition of this invention can consist essentially of a substituted methylenediphosphonic acid builder compound of this invention and a detergent surfactant in the ratios above described and the balance being a vehicle medium, for example, water, a water-alcohol mixture, etc.

In a finished detergent formulation of this invention there can be added in minor amounts materials which make the product more effective or more attractive. The following are mentioned only by way of example. A soluble sodium carboxymethyl cellulose can be added in minor amounts to inhibit soil redeposition. A tarnish inhibitor such as benzotriazole or ethylenethiourea can also be added in amounts up to about 2%. Fluorescers, perfume, and color while not essential in the compositions of the invention, can be added in amounts up to about 1%. An alkaline materials or alkali such as sodium hydroxide or potassium hydroxide can be added in minor amounts as supplementary pH adjusters. There might also be mentioned as suitable additives water, brightening agents, sodium sulfate, and sodium carbonate.

Corrosion inhibitors generally are added also. Soluble silicates are highly effective inhibitors and can be added to certain formulas of this invention at levels of from about 3% to about 8%. Alkali metal, preferably potassium or sodium, silicates having a weight ratio of $SiO_2:M_2O$ of from 1.0:1 to 2.8:1 can be used. M in this ratio refers to sodium or potassium. A sodium silicate having a ratio of $SiO_2:Na_2O$ of about 1.6:1 to 2.45:1 is especially preferred for economy and effectiveness.

In the embodiment of this invention which provides for a built liquid detergent, a hydrotropic agent may at times be found desirable. Suitable hydrotropes are water soluble alkali metal salts of toluenesulfonate, benzenesulfonate, and xylenesulfonate. Preferred hydrotropes are the potassium or sodium toluenesulfonates. The hydrotrope salt may be added, if desired, at levels of 0% to about 12%. While a hydrotrope will not ordinarily be found necessary it can be added, if so desired, for any reason such as to produce a product which retains its homogeneity at a low temperature.

The following compositions, in which the percentages are by weight, will serve to illustrate but not limit this invention. Each of the compositions in the examples gives in solution a pH within the desired range of from about 8 to about 12.

EXAMPLE IX

An excellent built liquid detergent formulation according to this invention has the following composition.

	Percent
Sodium dodecylbenzenesulfonate (the dodecyl radical being a polypropylene, predominantly tetrapropylene averaging 12 carbon atoms	6.0
Dimethyldodecylamine oxide	6.0
Trisodium ethylidenediphosphonate	20.0
Potassium toluenesulfonate	8.0
Sodium silicate (ratio SiO_2:Na_2O of 2.45:1)	3.8
Carboxymethyl hydroxyethyl cellulose	0.3
Water	Balance

Performance of this detergent composition is excellent in laundry tests as well as dishwashing evaluations. Its resistance to hydrolysis makes possible cleaner washes as well as longer shelf life since the novel builder compound remains in its active form throughout the complete washing cycle notwithstanding the large amounts of water present.

EXAMPLE X

An excellent granular detergent composition giving outstanding cleaning and whiteness maintenance results in washing situations contains the following ingredients in the weight percentages indicated:

	Percent
Sodium dodecylbenzenesulfonate (dodecyl group derived from tetrapropylene)	12.5
Tergitol 12-P-12 (condensation product of 12 moles of ethylene oxide with one mole of dodecyl phenol)	5.0
Trisodium isopropylidenediphosphonate	49.0
Sodium silicate (ratio SiO_2:Na_2O of 2:1)	6.0
Sodium sulfate	13.8
Water	Balance

EXAMPLE XI

A granular detergent composition prepared according to this invention has the following formulations:

	Percent
Sodium dodecylbenzenesulfonate (dodecyl group derived from tetrapropylene)	7.5
Pluronic L-64-F-68 Mixture[1]	2.0
Hydrogenated marine oil fatty acid	2.2
Tetrasodium monochloromethylenediphosphonate	59.6
Sodium silicate (ratio SiO_2:Na_2O of 2:1	9.7
Sodium sulfate	13.5
Water	Balance

[1] Condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol and having molecular weights of approximately 3,000 and 8,000, respectively.

Washing performance characteristics of this composition are exceptionally good from the point of view of general cleaning and whiteness maintenance performance.

EXAMPLE XII

Another highly effective granular detergent composition offering equally good laundering performance in the area of whiteness, cleaning and whiteness maintenance has the following formulation:

	Percent
Sodium dodecylbenzenesulfonate (dodecyl group derived from tetrapropylene)	20.0
1:1 mixture of hexadecyl-2-hydroxythiosulfate and octadecyl-2-hydroxythiosulfate	20.0
Trisodium dichloromethylenediphosphonate	20.0
Sodium silicate (ratio SiO_2:Na_2O of 2:1	5.0
Sodium sulfate	30.0
Water	5.0

EXAMPLE XIII

An effective cool water built liquid detergent which also performs exceptionally well as a heavy duty detergent composition especially in the areas of cleaning and whiteness maintenance, has the following composition:

	Percent
3(N,N - dimethyl-N-coconut ammonio)-2-hydroxypropane-1-sulfonate	12.0
Tripotassium ethylidenediphosphonate	20.0
Sodium silicate (SiO_2:Na_2O=1.6:1)	3.8
Potassium toluenesulfonate	8.5
Sodium carboxymethyl hydroxyethyl cellulose	.3
Fluorescent dye	.12
Perfume	.15
Benzotriazole	.02
Water	55.11

EXAMPLE XIV

An effective cool water built granular detergent composition according to this invention has the following composition:

	Percent
3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate	17.0
Tripotassium isopropylidenediphosphonate	45.0
Sodium silicate (SiO_2:Na_2O=2.5:1)	6.0
Sodium carboxymethyl cellulose	.3
Sodium sulfate	28.0
Water	3.5
Miscellaneous	Balance

Excellent whiteness maintenance and cleaning performance results are obtained by laundering with this composition.

Three different performance characteristics of the novel builder compounds of this invention were evaluated. These characteristics are cleaning, whiteness and whiteness maintenance. For purposes of this invention these terms have the following meanings. The term "cleaning" means the ability of a built laundering composition to remove deeply embedded soil lines or deposits such as occur on collars and cuffs. "Whiteness" is a more general term which is a measurement of the ability of a built laundering composition to whiten areas which are only slightly or moderately soiled. "Whiteness maintenance" is a term used to describe the ability of a built laundering composition of preventing the soil which has been removed from the fabrics during the washing cycle from redepositing back upon the fabrics. Specific test methods are described below.

The cleaning properties of the novel substituted methylenediphosphonic builder salts were discovered by washing naturally soiled white shirts with standardized detergency compositions built with different builder materials, including those of this invention. Shirts with detachable collars and cuffs were worn by male subjects under ordinary conditions for two normal working days. The collars and cuffs were then detached and washed in a small agitator type machine using aqueous solutions of the detergent compositions being evaluated. The specific washing conditions are described below.

After being washed and dried, the collars and cuffs were visually compared with other collars and cuffs, which had been similarly worn and soiled, but which were washed with a standard detergent composition. This visual comparison was made by a group of five people who were unfamiliar with the structure and purpose of the test and who formed their judgments independently. Their visual judgments were expressed on a scale ranging from zero to ten and the relative cleaning performances were thus noted.

Sodium tripolyphosphate and tetrapotassium pyrophosphate were employed in the tests due to their wide acceptance and use in the industry. These two compounds have come to be recognized somewhat as standards for builder compound performance. Compounds that equal or surpass these two compounds in builder performance are regarded as being worthwhile builders.

As representative of the novel class of builder compounds of this invention, the following compounds were selected and tested in this series of comparisons: trisodium ethylidenediphosphonate, trisodium isopropylidenephosphonate, and trisodium dichloromethylenediphosphonate. In this manner, the relative builder performance of the novel compounds of this invention was determined.

In this series of cleaning tests the detergent compositions consisted of a detergent surfactant and a builder. The concentration of the surfactant in the washing solution was constant at .03% by weight. The builders also were used in the washing solution at .03% concentration by weight.

The washing solutions had a pH of 10. The water contained seven grains (equivalent $CaCO_3$) per gallon hardness at a temperature of 140° F. and the washing cycle lasted 10 minutes.

The results of these cleaning tests are presented in Table I below:

Table I.—Cleaning evaluation using ABS[1] as the detergent surfactant at .03% concentration; temperature 140° F.

Builder compound (at 0.03% concentration)	Cleaning grades
(1) Trisodium ethylidenediphosphonate	2.9
(2) Trisodium isopropylidenediphosphonate	1.8
(3) Tetrapotassium pyrophosphate	1.4
(4) Trisodium dichloromethylenediphosphonate	.8
(5) Sodium tripolyphosphate	.7

[1] Sodium tetrapropylenebenzenesulfonate.

An examination of the performance data in Table I illustrates that each of the compounds of this invention that were tested as builders with ABS as a detergent surfactant performed either as well as or superior to sodium tripolyphosphate. Trisodium ethylidenediphosphonate and trisodium isopropylidenediphosphonate also scored higher than tetrapotassium pyrophosphate under the specific test conditions.

The absolute values presented in Table I are not significant in themselves. The primary significance of these data is to establish the relative performance of each of these compounds with regard to each other. Also, as noted previously, only the bare essentials of a built composition were used, namely, a detergent surfactant and a builder compound. Other well known detergency aids such as fluorescers and bleaches, etc., were not present in the test runs, so as not to mask over builder performance.

Further collar and cuff evaluations as described above were run with detergent surfactants other than ABS. The detergent surfactants which were employed in the washing solution at a concentration of .03% by weight were 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate, a 1:1 mixture of hexadecyl-2-hydroxythiosulfate and octadecyl-2-hydroxythiosulfate and Tergitol–12–P–12, which is a commercially available dodecyl phenyl polyethyleneglycol ether product prepared by condensing 12 moles of ethylene oxide with one mole of dodecyl phenol. Trisodium ethylidenediphosphonate (EDP) and sodium tripolyphosphate (STP) were used as builders. The EDP was used at a concentration in the wash water of .03% and STP was used at .03% and .06%. The temperature of the washing solution was 80° F. and was adjusted to a pH of 11 with sodium hydroxide. Again, the water hardness was seven grains per gallon and the washing cycle lasted ten minutes. The results are presented in Table II below:

TABLE II.—CLEANING EVALUATION

Detergent surfactants	Col. A, STP/.03%	Col. B, EDP/.03%	Col. C, STP/.06%
(1) Tergitol 12–P–12	3.9	6.4	6.1
(2) A mixture 1:1 of hexadecyl-2-hydroxythiosulfate and octadecyl-2-hydroxythiosulfate	4.1	5.8	6.8
sulfate and octadecyl-2-hydroxythiosulfate	4.1	5.8	6.8
(3) 3-(N,N-dimethyl-N-hexadecyl ammonio)-propane-1-sulfonate	7.5	8.4	7.4

It is apparent from Table II by comparing Column A with Column B that at equal builder concentrations of .03%, EDP scored substantially higher cleaning grades than STP with each of the detergent surfactants tested. Moreover, EDP performance at .03% compares favorably with STP at .06% concentration. The increased efficiency of EDP is thus illustrated under the test conditions employed.

The collar and cuff samples washed according to the compositions disclosed in Table II were also evaluated for "whiteness" performance in the following manner. "Whiteness" previously has been defined.

Whiteness measurements were made on the backs of the laundered naturally soiled cuffs with a commercially available photoelectric reflectometer, i.e. a Hunter Color and Color Difference Meter, manufactured by Gardner Laboratory, Inc., Bethesda, Maryland. This instrument is designed to distinguish color differences and operates on the tristimulus colorimeter principle wherein the 45° diffuse reflectance of an incident light beam on a test specimen is measured through a combination of green, blue and amber filters. The electrical circuitry of the instrument is so designed that lightness and chromaticity values for the test specimen are read directly. The departure from white (MgO taken as a standard white) of the test specimen is calculated by introducing the lightness and chromaticity values so obtained into a complex mathematical formula supplied by the manufacturer. An evaluation of relative performance compared to a standard detergent composition is thus obtained for the test formulations. These are later compared with other values obtained from other samples.

A more comprehensive description of this instrument and its mode of operation appears in a textbook entitled Color in Business, Science and Industry, by Deane B. Judd, pp. 260–262; published by John Wiley & Sons, New York (1952).

The data so obtained is presented in Table III below:

TABLE III.—WHITENESS EVALUATION RELATIVE TO STANDARD DETERGENT COMPOSITION; (NBS* UNITS)

Detergent surfactants	Col. A, STP/.03%	Col. B, EDP/.03%	Col. C, STP/.06%
(1) Tergitol 12–P–12	+.45	+.44	+.42
(2) 1:1 mixture of hexadecyl-2-hydroxythiosulfate and octadecyl-2-hydroxythiosulfate	+.28	+.55	+.55
(3) 3-(N,N-dimethyl-N-hexadecyl ammonio) propane-1-sulfonate	+.37	+.96	+.57
(4) Standard composition: Tetrapropylenebenzenesulfonate (140° F.)			0

*National Bureau of Standards Unit.

The whiteness figures presented in Table III, above, illustrate the excellent whiteness results obtained with EDP-built laundering compositions with several different surfactants. Higher figures indicate better whiteness levels. It should be noted that for equal weight concentrations of the respective builder materials, i.e. .03% STP and EDP, the EDP whiteness values are either comparable with Tergitol as the detergent surfactant or are very substantially better, as with the second and third detergent surfactants in Table III. (Compare Column A with Column B.) Moreover, a comparison between Column B and Column C shows that whiteness results obtained with EDP at .03% concentration compare very favorably with whiteness results obtained with STP at .06% concentration. EDP is thus shown to be a highly more efficient builder than STP with several different detergents surfactants under the specific test conditions.

Unsoiled swatches of cotton terry cloth were washed along with the soiled collars and cuffs in Examples VI and VII to arrive at an independent evaluation of the whiteness maintenance property of the built laundering composition being tested. Soil appearing on the cotton terry cloth swatches after being washed along with the soiled fabrics, represents soil which was removed from the soiled fabrics, suspended in the washing solution and the redeposited on the terry cloth swatches. This type of redeposited soil on the fabrics is of serious concern and improvements in this area are constantly being sought.

The same measuring procedure was followed in this evaluation as in the measurement of whiteness in Table III. The Hunter Color and Color Difference Meter was again used and the figures in Table IV below, are whiteness units as calculated from data obtained by grading the washed and dried cotton terry cloth. Increasing values again represent better results.

TABLE IV.—WHITENESS MAINTENANCE EVALUATION RELATIVE TO STANDARD DETERGENT COMPOSITION; TEMPERATURE 80° F. (NBS* UNITS)

Detergent surfactants	Col. A, STP/.03%	Col. B, EDP/.03%	Col. C, STP/.06%
(1) Tergitol 12-P-12	+.79	+.88	+.54
(2) 1:1 mixture of hexadecyl-2-hydroxy thiosulfate and octadecyl-2-hydroxythiosulfate	+.50	+.87	+.60
(3) Standard Composition: Tetrapropylene benzene sulfonate (140° F.)			0

*National Bureau of Standards.

The whiteness maintenance results obtained with EDP at .03% are substantially superior to the whiteness maintenance results attained by STP at .03% with each of the two different surfactants tested. Even more surprising, however, are the better whiteness maintenance values of EDP at .03%, Column B, over the results using STP at .06% concentration. There is no sound basis for expecting this superior performance by EDP over STP in such an important detergency area as whiteness maintenance.

The preceding laundering tests illustrate the excellent over-all detergency results attained with the novel builder compounds of this invention based on comparisons with a sodium tripolyphosphate builder. Moreover, similarly good performance results in areas of cleaning, whiteness and whiteness maintenance are obtained when the substituted methylenediphosphonate compounds of this invention are employed to build other detergent surfactants besides those for which performance data is presented above. While not complete, a list of suitable soap and synthetic non-soap detergent compounds which can be used appears above. Furthermore, the novel compounds described herein can be used alone as detergent builders, or they can be used in admixtures with other organic and inorganic builder materials.

Though the principles of this invention have been illustrated herein by means of certain specific examples and tests, it is not intended that the scope of the invention be

limited thereby, but only as indicated in the following claims.

What is claimed is:

1. A detergent composition consisting essentially of an organic detergent selected from the group consisting of anionic detergents selected from the group consisting of

(a) fatty acid soaps, and

(b) water-soluble alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl radical having 8 to 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals;

nonionic detergents;

ampholytic detergents selected from the group consisting of

(a) sodium-3-dodecylaminopropionate, and

(b) sodium - 3 - dodecylaminopropanesulfonate; and zwitterionic detergents which are aliphatic quaternary ammonium compounds containing straight chain or branched chain aliphatic radicals, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group which is carboxy, sulfo, or sulfato, and mixtures thereof, and

as a detergency builder, a compound selected from the group consisting of the water-soluble salts of ethyldidenediphosphonic acid, isopropylidenediphosphonic acid, benzylmethylenediphosphonic acid, bis(benzyl)methyldenediphosphonic acid, monochloromethylenediphosphonic acid, dichloromethylenediphosphonic acid, monobromomethylenediphosphonic acid, dibromoethylenediphosphonic acid, monofluoromethylenediphosphonic acid, difluoromethylenediphosphonic acid, 2-carboxyethylidenediphosphonic acid, bis(carboxymethyl)methylenediphosphonic acid, the water-soluble salts being selected from the group consisting of sodium, potassium, ammonium and substituted ammonium salts, wherein the ratio by weight of said builder to said detergent is in the range of from about 1:3 to about 10:1, said composition providing in an aqueous solution a pH of from about 8 to about 12.

2. A detergent composition according to claim **1** wherein the ratio by weight of said builder to said detergent is within the range of from about 1:2 to about 5:1, and provides in aqueous solution a pH of about 9.5 to 11.5.

3. A detergent composition according to claim **1** wherein the anionic detergent is a water-soluble alkali metal salt of an organic sulfuric reaction product having in its molecular structure an alkyl radical having 8 to 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals.

4. A detergent composition according to claim **1** wherein the anionic detergent is an alkali metal alkyl sulfate compound in which the alkali metal is selected from sodium and potassium and in which the alkyl substituent contains from about 8 to 18 carbon atoms.

5. A detergent composition accordng to claim **1** wherein the anionic detergent is an alkali metal alkylbenezenesulfonate in which the alkali metal is selected from sodium and potassium and in which the alkyl group contains from about 9 to about 15 carbon atoms.

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