

1

3,562,166

BUILT DETERGENT COMPOSITIONS

Denzel Allan Nicholson, Springfield Township, Hamilton County, Ohio, and Darrel Campbell, King of Prussia, Pa., assignors to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio
No Drawing. Filed Dec. 24, 1968, Ser. No. 786,766

Int. Cl. C11d 3/36

U.S. Cl. 252-152

9 Claims

ABSTRACT OF THE DISCLOSURE

Built detergent compositions containing an organic synthetic detergent and a builder which is ethane-1,2-dicarboxy-1,2-diphosphonic acid, ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonic acid, ethene-1,2-dicarboxy-1-phosphonic acid, and dialkyl (P,P')ethane-1,2-dicarboxy-1,2-diphosphonic acid or alkali metal or ammonium salts thereof in a proportion of detergent to builder of 5:1 to about 1:20.

FIELD OF THE INVENTION

This invention relates to built detergent compositions which are useful in household laundry situations. Built detergent compositions have many uses, however, including dishwashing and other household washing and cleaning applications such as washing soiled walls and floors.

The use of builder compounds as adjuncts to soap and synthetic detergents is widespread. The property of some compounds to improve the cleaning levels of detergents is a well-known phenomenon. Notwithstanding the fact that this property is widely known, a complete explanation of how builders perform and function still has not been provided. A set of criteria does not exist which would permit one to predict which compounds possess significant builder properties in actual detergency systems.

Builder compounds are thought to have some effect in such diverse areas of detergency evaluation as stabilization of soil suspension, emulsification of soil particles, the surface activity of aqueous solutions, foaming or suds-producing characteristics of washing solutions, peptization of soil agglomerates, neutralization of acid soil, and the inactivation of mineral constituents present in the washing solution (so-called sequestering or water softening). This list is not all inclusive since other properties of builder compounds are known. The point to be understood is that no general basis has been found either as regards physical properties or chemical structure by which one might, with certainty, predict the suitability of chemical materials as builders for detergent compositions.

The known compounds which have been found useful as builders can be categorized generally into inorganic and organic alkaline builder salts. An example of the inorganic type is sodium tripolyphosphate which is perhaps the most widely known and commercially used detergency builder. Other examples of inorganic alkaline builders are sodium pyrophosphate which is also commercially used as well as other alkali metal carbonates, borates, phosphates, silicates and the like.

Alkali metal salts of nitrilotriacetic acid, ethylenediaminetetraacetic acid, ethane-1-hydroxy-1,1-diphosphonic acid, and ethane-1-hydroxy-1,1,2-triphosphonic acid are examples of organic alkaline builders.

It is common to employ mixtures of such organic and inorganic compounds in commercially available built detergent compositions. Each of the known builder compounds in both the inorganic and organic classes appear to have certain advantages and disadvantages. The need for, and interest in, providing suitable alternatives and replacements for known builders underscores continued

2

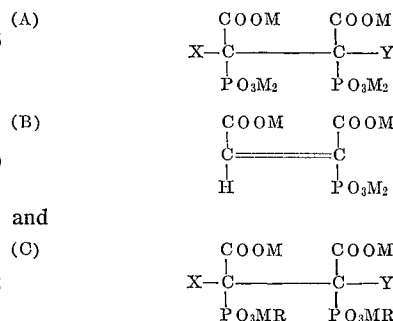
research and development efforts for improved detergency builder compounds.

SUMMARY OF THE INVENTION

It has now been discovered that organic compounds containing both carboxy and phosphonate groups in certain critical positions in the molecule are effective detergency builders. Accordingly, the present invention pertains to detergent compositions comprising an organic synthetic detergent and a detergency builder ingredient selected from one of the newly discovered classes of builder compounds described herein. The present invention provides as novel classes of builders ethane-1,2-dicarboxy-1,2-diphosphonic acid, ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonic acid, ethene-1,2-dicarboxy-1-phosphonic acid and a diester of ethane-1,2-dicarboxy-1,2-diphosphonic acid, and the alkali metal and ammonium salts of these acids.

DETAILED DESCRIPTION OF THE INVENTION

The present invention pertains to detergent compositions which comprise an organic synthetic detergent and a builder ingredient selected from the group consisting of:



in which M is hydrogen, alkali metal or ammonium and R is an alkyl group having 1 to about 6 carbon atoms, and X and Y are each hydrogen or hydroxy.

Of the three groups of builder compounds, members of group A are preferred and provide detergency builder results superior to the other two groups of builder compounds. The preferred group A builders are dicarboxy diphosphonate compounds and dicarboxy dihydroxy diphosphonate compounds. Group B consists of unsaturated ethene compounds containing two vicinal carboxy groups and one phosphonate group. Group C builder compounds are partial (di)ester compounds. It is totally unexpected that ester compounds of any structure would perform as builder compounds. While they are less efficient than either of the other two groups, the Group C builders provide an alternative of satisfactory performance to detergent formulations. Esters are generally not known to be builders for detergent compositions. Each of these three classes is described in detail.

GROUP A BUILDERS

Dicarboxy diphosphonate builder compounds

The following compounds are illustrative of the Group A detergent builders provided of the present invention:

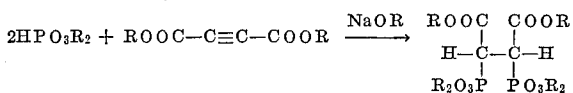
ethane-1,2-dicarboxy-1,2-diphosphonic acid;
sodium ethane-1,2-dicarboxy-1,2-diphosphonate;
dipotassium ethane-1,2-dicarboxy-1,2-diphosphonate;
tri ammonium ethane-1,2-dicarboxy-1,2-diphosphonate;
tetralithium ethane-1,2-dicarboxy-1,2-diphosphonate;
pentasodium ethane-1,2-dicarboxy-1,2-diphosphonate;
hexapotassium ethane-1,2-dicarboxy-1,2-diphosphonate;
disodium diammonium ethane-1,2-dicarboxy-1,2-diphosphonate;
pentaammonium ethane-1,2-dicarboxy-1,2-diphosphonate;

ammonium ethane-1,2-dicarboxy-1,2-diphosphonate;
 pentapotassium ethane-1,2-dicarboxy-1,2-diphosphonate;
 ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonic
 acid;
 sodium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphos-
 phonate;
 dipotassium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-di-
 phosphonate;
 trilitium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphos-
 phonate;
 tetraammonium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-
 diphosphonate;
 pentasodium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-di-
 phosphonate;
 hexapotassium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-
 diphosphonate;
 diammonium disodium ethane-1,2-dicarboxy-1,2-dihy-
 droxy-1,2-diphosphonate;
 trisodium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-di-
 phosphonate;
 tetrasodium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-di-
 phosphonate;
 sodium triammonium ethane-1,2-dicarboxy-1,2-dihy-
 droxy-1,2-diphosphonate;
 ethane-1,2-dicarboxy-1-hydroxy-1,2-diphosphonic acid
 and
 ethane-1,2-dicarboxy-2-hydroxy-1,2-diphosphonic acid.

Members of the Group A class of builders can be pre-
 pared in any convenient manner. For example, a reaction
 described by Pudovik in "Soviet Research on Organo-
 Phosphorus Compounds," 1949-1956, Part III, 547-85c
 is used to prepare an ester of ethane - 1,2 - dicarboxy-1,2-
 diphosphonic acid which is, by ordinary hydrolysis reac-
 tions, then converted to the free acid form. Neutraliza-
 tion by base, e.g., alkali, compounds such as sodium hy-
 droxide, potassium hydroxide, carbonates and the like are
 used to prepare a desired salt of the acid.

Other members of the Group A builder compounds are
 the subject of a separate copending, commonly assigned
 patent application Ser. No. 786,765, filed Dec. 24, 1968,
 being filed concurrently with this application. The title of
 the application is "Ethane - 1,2 - Dicarboxy - 1,2-Dihy-
 droxy - 1,2 - Diphosphonic Acid, Lower Alkyl Esters, Al-
 kali Metal Salts Thereof And Process For Preparing
 Same" by D. Allan Nicholson and Darrel Campbell. That
 application is incorporated herein by reference. Exam-
 ples of preparing such compounds are given below.

The following example illustrates a typical preparation
 for dicarboxy diphosphonate members of this class of
 builder compounds. It involves a sodium alkoxide cata-
 lyzed addition of two moles of dialkylphosphite to an
 ester of acetylenedicarboxylic acid. A general reaction for
 this reaction is given below:



EXAMPLE I

Ethane-1,2-dicarboxy-1,2-diphosphonic acid

Six moles, 853 gms. of the dimethyl ester of acetylene-
 dicarboxylic acid, $\text{CH}_3\text{O}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$, was combined
 with 300 ml. of toluene in a dry 3 liter, 3-necked flask,
 which was fitted with a magnetic stirrer, a thermometer, a
 500 ml. addition funnel, and a water cooled Allihn con-
 denser. The solution was heated to 120° C., and the heat-
 ing mantle removed while 14 moles, 1945 gms., of di-
 ethyl phosphite, $\text{HPO}_3\text{C}_2\text{H}_5$, was added dropwise over a
 one hour period. The heat evolved was sufficient to main-
 tain a steady reflux rate of the toluene at 135° C. during
 the addition period. After heat evolution ceased, the heat-
 ing mantle was again applied to keep the reaction tem-
 perature at 135° C. for 4 hours. The product was then
 distilled to separate the unreacted starting reagents from
 the dimethyl tetraethyl ester of ethane - 1,2 - dicarboxy-

1,2-diphosphonic acid. A total of 2023 gms. (80% yield)
 of the dimethyl tetraethyl ester of ethane - 1,2 - dicarboxy-
 1,2-diphosphonic acid was recovered, B.P. 175°-180° at
 75-150 μ pressure, n_D^{25} 1.4535, d_4^{25} 1.225. The ^{31}P MR
 spectrum of this material gave a single unresolved peak
 at δ = -18.6 p.p.m.

Analysis.—Calcd. for $\text{C}_{14}\text{H}_{28}\text{O}_{10}\text{P}_2$ (percent): C, 40.2;
 H, 6.75; P, 14.8. Found (percent): C, 40.4; H, 6.5; P,
 15.1. Molecular weight determined on a 3D 1 A Mechro-
 lab Osmometer—420 (theory 418.3).

A sample of the ester was converted to the acid by
 refluxing for 4 hours with a 100% molar excess of con-
 centrated HCl. The acid solution was evaporated under
 vacuum to give a white solid which was twice recrystal-
 lized from 1:10:23 water:acetone:ether. The product,
 ethane - 1,2 - dicarboxy - 1,2-diphosphonic acid, M.P.
 209-210°, gave a peak δ = -15.0 p.p.m. in the ^{31}P MR
 spectrum.

Analysis.—Calcd. for $\text{C}_4\text{H}_8\text{O}_{10}\text{P}_2$ (percent): C, 17.3;
 H, 2.9; P, 22.3. Found (percent): C, 17.4; H, 3.7; P, 22.4.

EXAMPLE II

Sodium ethane-1,2-dicarboxy-1,2-diphosphonate

A 0.136 gram sample (0.0004895 mole) of ethane-1,2-
 dicarboxy - 1,2 - diphosphonic acid was titrated with
 0.1005 N NaOH. Two sharp endpoints were noted: the
 first at pH 4.5, using 9.65 ml. of base (0.9698 meq., cal-
 culates to $\text{Na}_{1.98}$ salt); the second endpoint at pH 8.5,
 using a total of 19.0 ml. of base (1.9195 meq., calculates
 to $\text{Na}_{3.92}$ salt).

A larger sample of the acid was titrated to the Na_4H_2
 salt. The white solid recovered was crystallized once from
 8:3:1 water:acetone:ether and twice from water:acetone
 alone. ^{31}P MR data could not be obtained because of the
 low solubility (see Table I) of the sodium salt.

Analysis.—Calcd. for $\text{C}_4\text{H}_8\text{O}_{10}\text{P}_2\text{Na}_4$ (percent): C,
 13.1; H, 1.1; P, 16.9. Found (percent): C, 13.8; H, 2.1;
 P, 16.7.

Ethane - 1,2 - dicarboxy - 1,2-dihydroxy-1,2-diphos-
 phonic acids are prepared by a reaction between an ester
 of ethane - 1,2 - dicarboxy - 1,2-diphosphonic acid and an
 alkali metal hypohalite. The reaction product of this re-
 action is an epoxide ester compound which can be readily
 converted to a dihydroxy ester, an acid or a salt. The re-
 action between the alkali metal hypohalite and the ester
 of ethane-1,2 - dicarboxy-1,2-diphosphonic acid requires
 about stoichiometric amounts of each reactant, i.e., about
 2 moles of hypohalite to each mole of the ester. Propor-
 tions can be used in the range of 1.75:1 to about 2.5:1.

The following procedure is presented to illustrate a
 suitable way to prepare the members of this class of com-
 pounds. A more complete disclosure is found in the afore-
 mentioned patent, a copending, concurrently filed applica-
 tion of Nicholson and Campbell which is incorporated by
 reference.

EXAMPLE III

Pentasodium ethane-1,2-dicarboxy-1,2-dihydroxy- 1,2-diphosphonate

To 1,155 cc. of a 5.25% NaOCl solution was added
 155.4 g. of tetraethyl dimethyl ethane-1,2-dicarboxy-
 1,2-diphosphonate. The temperature of the resulting solu-
 tion rose to 55° C. and was maintained there for 2 hours.
 After cooling to room temperature, the solution was ex-
 tracted 5 times with 300 cc. portions of CHCl_3 . Removal
 of the CHCl_3 left a colorless liquid weighing 152.4 g.
 Analysis proved the product to be a nearly quantitative
 yield of an epoxide compound, dimethyltetraethyl(P,P')-
 1,2-oxo-1,2-dicarboxy-1,2-diphosphonate ^{31}P MR spec-
 trum: δ = -7.9 p.p.m. (multiplet).

Analysis.—Calcd. (percent): C, 38.9; H, 6.1; P, 14.3;
 molecular weight 432. Found (percent): C, 38.2; H, 5.9;
 P, 14.5; molecular weight 475.

The sodium hypochlorite solution can be replaced
 with an equivalent amount of sodium hypobromite or po-

tassium hypochlorite and the corresponding sodium and potassium salts are obtained in quantitative yields. The tetraethyl dimethyl ester can be replaced by equivalent amounts of hexamethyl, hexaethyl and hexahexyl groups and the reaction proceeds in a satisfactory manner.

The dimethyltetraethyl(P,P')-1,2-oxo-1,2-dicarboxy-1,2-diphosphonate reaction product was dissolved in an equal amount of $n\text{-Bu}_2\text{O}$, the solution heated to 105° and HBr passed through for 7 hours. At the end of this period two layers were present. Extraction with water separated the bottom layer and the $n\text{-Bu}_2\text{O}$ layer was discarded. Removal of the water left a colorless oil which was dissolved in a solution of 44.4 g. NaOH (1.11 mole) in water. This solution was heated to 60°C , methanol added to bring to the cloud point, and on cooling a white precipitate formed. The ^{31}P MR spectrum of this solid, $\delta = -6.0$ p.p.m. (broad), indicated that all ester groups had not been removed. Therefore, it was hydrolyzed by boiling 2 hours with HCl (50/50 HCl + water). After removal of excess HCl, a water solution of the oil which remained was titrated to pH—9 at 60°C . On cooling, a white solid was collected which analysis proved to be pentasodium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonate.

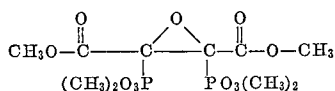
The total solid collected weighed 34.2 g. (22.6%). ^{31}P MR spectrum: $\delta = -6.7$ p.p.m. (singlet).

Analysis.—Calcd. for $\text{C}_4\text{H}_3\text{O}_{12}\text{P}_2\text{Na}_5$ (percent): C, 11.4; H, 0.7; P, 14.7; Na, 27.4. Found (percent): C, 13.4; H, 0.6; P, 15.0; Na, 27.6.

EXAMPLE IV

Ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonic acid

One mole (362 g.) of hexamethyl ester of ethane-1,2-dicarboxy-1,2-diphosphonate are combined with a solution containing 2 moles of sodium hypobromite dissolved in one liter of water. This solution is stirred for 15 minutes and then extracted three times with CCl_4 . Removal of the CCl_4 leaves about 260 g. of a substantially pure epoxide ester reaction product



This epoxide is combined with 500 cc. of a 50/50 mixture of concentrated hydrogen chloride and water and the solution is heated to 90°C . for 3 hours. Following removal of the hydrogen chloride and excess water the remaining product is an oily product. This is redissolved in water and 7 equivalents of sodium hydroxide are added. The mixture is heated to 70°C . for 30 minutes. The resulting solution is passed through an ion-exchange column to yield an aqueous solution of ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonic acid. The water is evaporated leaving the substantially pure acid as a viscous liquid.

EXAMPLE V

Tripotassium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonate

Dimethyl tetraethyl-1,2-oxo-1,2-dicarboxy-1,2-diphosphonate (1 mole, 432 g.) is combined with 40 g. (1 mole) of NaOH in 1 liter of water and the mixture is heated to 75°C . for 30 minutes. To this solution 1000 cc. of concentrated HCl are added and the total solution is refluxed for $2\frac{1}{2}$ hours. After removal of excess HCl and most of the water, (leaving about 250 cc. of final solution) the solution is ion-exchanged to remove the sodium ions. Again the solvent is removed, this time to dryness. The resulting viscous liquid is combined with 168.3 g. (3 moles) of KOH in 500 cc. of water. Removal of water leaves tripotassium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonate in a substantially pure form.

GROUP B BUILDER COMPOUNDS

Dicarboxy monophosphonates

The compounds of this class of builders are the subject of a separate copending, commonly assigned, patent application Ser. No. 786,764 filed Dec. 24, 1968 being filed concurrently with this application by Nicholson and Campbell. The title is "Ethene-1,2-Dicarboxy-1-Phosphonic Acid, Esters And Salts Thereof, And Process For Preparing Same." The disclosure of that application is incorporated herein by reference.

Specific compounds illustrative of Group B builders are:

- ethene-1,2-dicarboxy-1-phosphonic acid;
- sodium ethene-1,2-dicarboxy-1-phosphonate;
- dipotassium ethene-1,2-dicarboxy-1-phosphonate;
- trilithium ethene-1,2-dicarboxy-1-phosphonate;
- tetraammonium ethene-1,2-dicarboxy-1-phosphonate;
- disodium diammonium ethene-1,2-dicarboxy-1-phosphonate;
- ammonium ethene-1,2-dicarboxy-1-phosphonate;
- disodium ethene-1,2-dicarboxy-1-phosphonate;
- tripotassium ethene-1,2-dicarboxy-1-phosphonate; and
- tetrasodium ethene-1,2-dicarboxy-1-phosphonate.

The compounds of Group B can be prepared by reacting a dialkyl phosphite compound with a lower alkyl ester of acetylenedicarboxylic acid at a temperature of from about 90°C . to about 140°C . The following procedure illustrates a satisfactory method for preparing compounds in this class of builders. A more complete description is presented in the copending application mentioned above in the discussion of Group B Builder Compounds.

EXAMPLE VI

Ethene-1,2-dicarboxy-1-phosphonic acid and the trisodium salt

Dimethyl acetylenedicarboxylate (426 g., 3 moles) was placed in a 1 liter, 3-necked flask fitted with a mechanical stirrer and a condenser and heated to 105°C . To this solution was added dropwise 330 g. (3 moles) of dimethyl hydrogen phosphite. The reaction temperature was maintained at $100\text{--}110^\circ$ by cooling and control of the drop rate. Addition was complete after about 1 hour. The reaction mixture was then distilled yielding tetramethyl ethene-1,2-dicarboxy-1-phosphonate (B.P. at $17\text{--}19^\circ$, $112\text{--}115^\circ\text{C}$., 255.9 g., 34%) $n_D^{25} = 1.4586$.

Analysis: Calcd. for $\text{C}_6\text{H}_{13}\text{O}_7\text{P}$ (percent): C, 38.2; H, 5.2; P, 12.3; molecular weight 252. Found (percent): C, 38.1; H, 5.2; P, 12.4; molecular weight 250. ^{31}P MR spectrum: $\delta = -12.0$ p.p.m. (multiplet).

A solution was prepared containing 77.9 g. (0.31 mole) of tetramethyl ethene-1,2-dicarboxy-1-phosphonate ester in 500 cc. of 50/50 concentration HCl/water. The solution was refluxed 3 hours, the solvent and excess HCl removed by flash evaporation. A reaction product was formed containing ethene-1,2-dicarboxy-1-phosphonic acid (^{31}P MR spectra—13.0; multiplet). The crude reaction product containing the free acid was dissolved in a solution consisting of 37.1 g. NaOH (0.93 mole) in water. This solution was flash evaporated and the resulting oil induced to solidify by azeotroping with toluene. A total of 43.2 g. of trisodium ethene-1,2-dicarboxy-1-phosphonate were obtained. This compound was purified by forcing it out of a water solution with methanol and then leaching the solid with boiling methanol.

Analysis: Calcd. for $\text{C}_4\text{H}_2\text{O}_7\text{PNa}_3$ (percent): C, 18.3; H, 0.8; P, 11.8; Na, 26.3; molecular weight 261.9. Found (percent): C, 17.1; H, 1.7; P, 11.7; Na, 26.1.

GROUP C BUILDER COMPOUNDS

Partial esters of ethane-1,2-dicarboxy-1,2-diphosphonate compounds

This group of builder compounds comprises dialkyl (P,P')ethane-1,2-dicarboxy-1,2-diphosphonate compounds

in which the alkyl group contains from 1 to about 6 carbon atoms.

This class of compounds is illustrated by the following specific examples:

diethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate;
trisodium dimethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate;
sodium dimethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate;
diammonium dipropyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate;
tetrasodium dipentyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate;
trilithium diisopropyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate;
tripotassium dimethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate;
disodium diethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate;
disodium diammonium dipropyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate; and
ammonium dibutyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate.

A procedure for preparing compounds of this class is presented below.

EXAMPLE VII

Tetrasodium dimethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate

When a hexamethyl ester of ethane-1,2-dicarboxy-1,2-diphosphonic acid is refluxed with an excess of NaOH, complete hydrolysis to the hexasodium salt occurs. It is possible to prepare tetrasodium dimethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate by refluxing the hexamethyl ester of ethane-1,2-dicarboxy-1,2-diphosphonic acid with 4 equivalents of NaOH.

A solution of 42.7 g. (0.126 mole) of hexamethyl ethane-1,2-dicarboxy-1,2-diphosphonate was dissolved in 250 cc. of water and 20.2 g. of NaOH (0.504 mole) was added. The resulting solution was refluxed for 4 hours, protection from the atmosphere being accomplished with an Ascarite tube. At the end of the heating period there was a small amount of yellow solid in the flask. This was removed by filtration and discarded. Removal of the water left an oil which was dried by azeotrope with benzene for several hours. The solid which was formed was collected and washed 4 times with hot methanol and then with acetone. After drying at 25 μ there remained 42.7 g. of a white solid (86%) which was tetrasodium dimethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate. $P^{31}MR$ spectrum: $\delta = -16.4$ p.p.m. (doublet).

Analysis: Calcd. for $C_6H_8O_{10}P_2Na_4$ (percent): C, 18.3; H, 2.0; P, 15.7; Na, 23.4. Found (percent): C, 17.8; H, 2.3; P, 15.8; Na, 22.7.

Instead of starting with a hexamethyl ester, it is possible to start with a hexaethyl, hexapropyl, hexabutyl, hexapentyl, hexahexyl ester and the like or a combination of esters such as dimethyl tetraethyl. The result in each case will be the corresponding dialkyl ester of ethane-1,2-dicarboxy-1,2-diphosphonic acid.

A built detergent composition prepared according to the present invention comprises a detergent and a builder described herein in a ratio, by weight, of from about 5:1 to about 1:20 and, preferably, in a weight ratio of detergent to builder of from 2:1 to about 1:10. It is customary to speak of the ingredients in detergent compositions as being by weight. By way of example, a detergent composition prepared according to the present invention in which the detergent to builder ratio is about 4:1 to 1:1 on a weight basis is especially useful as a dishwashing composition or a fine fabric laundering composition. A detergent composition having a detergent to builder ratio of 1:1 to 1:1.9 has excellent performance characteristics for

washing lightly soiled items in an ordinary household wash. Yet further by way of illustration, heavily soiled fabrics are most effectively laundered with built detergent compositions in which the detergent to builder ratio is from about 1:2 to about 1:20. Little additional benefit is gained by increasing the proportion of builder up to a ratio of 1:20.

In practicing the present invention, at least one detergent compound having the desired sudsing, cleaning, mildness characteristics and the like, is mixed with effective amount of a builder compound of this invention in the useful by-weight proportions set forth above. The detergent portion of the built composition also can, and generally does, comprise a mixture of two or more detergents. The builder portion likewise can also comprise a mixture of two or more builder compounds.

The specific performance properties of the built compositions of this invention vary to some extent depending upon the ratio of the detergent to the builder. Inasmuch as mixtures of detergents can be used, as well as mixtures of the builders described herein (with each other and also with previously known builders) performance variation can be expected. Moreover, there will be considerable variation in the strength of the washing solutions employed by different consumers, i.e., some housewives tend to use more or less of the built detergent composition than will others. Variations in temperature and soil loads will occur. The degree of hardness of the water used to make up the washing solution will also bring about apparent differences in the cleaning power and whiteness maintenance results. Different fabrics respond in somewhat different ways to different detergent compositions. The best type of built detergent composition for household use is a composition which accomplishes an excellent cleaning and whiteness maintenance effect under the most diverse cleaning conditions. It is in this respect that the built detergent compositions of this invention are especially useful.

The detergents with which the builder compounds described herein can be used include water soluble anionic, nonionic, ampholytic and zwitterionic detergent compounds, or mixtures of compounds selected from these general classes of detergents. Each of these classes is illustrated below.

(A) Anionic soap and non-soap synthetic detergents

This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Suitable fatty acids can be obtained from natural sources such as, for instances, from plant or animal esters (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease, lard, and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Napthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. 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.

This class of detergents also includes 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 sulfonic acid or sulfuric acid ester radical. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Examples of this group of synthetic detergents which form a part of the preferred built

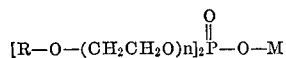
detergent compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, especially those of the type described in United States Letters Patents Numbers 2,220,099 and 2,477,383; sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; 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 alkyl phenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 8 to about 12 carbon atoms.

Additional examples of anionic non-soap synthetic detergents which come within the terms of the present invention are 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 methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in United States Letters Patents 2,486,921; 2,486,922; and 2,396,278.

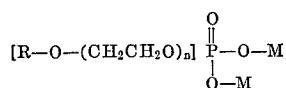
Still other anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfo succinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfo-succinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl ester of sodium sulfosuccinic acid.

Anionic phosphate surfactants are also useful in the present invention. These are surface active materials having substantial detergent capability in which the anionic solubilizing group connecting hydrophobic moieties is an oxy acid of phosphorus. The more common solubilizing groups, of course, are $-SO_3H$, $-SO_3H$, and $-CO_2H$. Alkyl phosphate esters such as $(R-O)_2PO_2H$ and $ROPO_3H_2$ in which R represents an alkyl chain containing from about 8 to about 20 carbon atoms are useful.

These esters can be modified by including in the molecule from one to about 40 alkylene oxide units, e.g., ethylene oxide units. Formulae for these modified phosphate anionic detergents are:



or



in which R represents an alkyl group containing from about 8 to 20 carbon atoms, or an alkylphenyl group in which the alkyl group contains from about 8 to 20 carbon atoms, and M represents a soluble cation such as hydrogen, sodium, potassium, ammonium or substituted ammonium; and in which n is an integer from 1 to about 40.

A specific anionic detergent which has also been found excellent for use in the present invention is described more fully in the U.S. Pat. 3,332,880 of Phillip F. Pflaumer and Adriaan Kessler, issued July 25, 1967. This anionic detergent consists essentially of from about 30% to about 70% of Component A, from about 20% to about 70% of Component B, and from about 2% to about 15% of Component C, wherein:

(a) Said Component A is a mixture of double-bond positional isomers of water soluble salts of alkene-1-sulfonic acids, containing from about 10 to about 24 carbon atoms, said mixture of positional isomers including about 10% to about 25% of an alpha-beta unsaturated isomer, about 30% to about 70% of a beta-gamma unsaturated isomer, about 5% to about 25% of a gamma-delta unsaturated isomer, and about 5% to about 10% of a delta-epsilon unsaturated isomer;

(b) Said Component B is a mixture of water soluble salts of bifunctionally-substituted sulfur-containing saturated aliphatic compounds containing from about 10 to about 24 carbon atoms, the functional units being hydroxy and sulfonate radicals with the sulfonate radical always being on the terminal carbon and the hydroxyl radical being attached to a carbon atom at least two carbon atoms removed from the terminal carbon atom, at least 90% of the hydroxy radical substitutions being in 3, 4, and 5 positions; and

(c) Said Component C is a mixture comprising from about 30-95% water soluble salts of alkene disulfonates containing from about 10 to about 24 carbon atoms, and from about 5% to about 70% water soluble salts of hydroxy disulfonates containing from about 10 to about 24 carbon atoms, said alkene disulfonates containing a sulfonate group attached to a terminal carbon atom and a second sulfonate group attached to an internal carbon atom not more than about six carbon atoms removed from said terminal carbon atom, the alkene double bond being distributed between the terminal carbon atom and about the seventh carbon atom, said hydroxy disulfonates being saturated aliphatic compounds having a sulfonate radical attached to a terminal carbon, a second sulfonate group attached to an internal carbon atom not more than about six carbon atoms removed from said terminal carbon atom, and a hydroxy group attached to a carbon atom which is not more than about four carbon atoms removed from the site of attachment of said second sulfonate group.

(B) Nonionic synthetic detergents

Nonionic synthetic detergents may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

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 a 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 1500 to 1800. 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 alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, or nonene, for example.

(2) Those derived from the condensation of ethylene

11

oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. 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 ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(4) Nonionic detergents include nonyl phenol condensed with either about 10 or about 30 moles of ethylene oxide per mole of phenol and the condensation products of coconut alcohol with an average of either about 5.5 or about 15 moles of ethylene oxide per mole of alcohol and the condensation product of about 15 moles of ethylene oxide with one mole of tridecanol.

Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; dodecyl mercaptan condensed with 10 moles of ethylene oxide per mole of mercaptan; bis-(N-2-hydroxyethyl) lauramide; nonyl phenol condensed with 20 moles of ethylene oxide per mole of nonyl phenol; myristyl alcohol condensed with 10 moles of ethylene oxide per mole of myristyl alcohol; lauramide condensed with 15 moles of ethylene oxide per mole of lauramide; and di-iso-octylphenol condensed with 15 moles of ethylene oxide.

(5) A detergent having the formula $R^1R^2R^3N \rightarrow O$ (amine oxide detergent) wherein R^1 is an alkyl group containing from about 10 to about 28 carbon atoms, from 0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of R^1 which is an alkyl group containing from about 10 to about 18 carbon atoms and 0 ether linkages, and each R^2 and R^3 are selected from the group consisting of alkyl radicals and hydroxyalkyl radicals containing from 1 to about 3 carbon atoms;

Specific examples of amine oxide detergents include:

dimethyldodecylamine oxide
dimethyltetradecylamine oxide
ethylmethyltetradecylamine oxide
cetyldimethylamine oxide
dimethylstearylamine oxide
cetyllethylpropylamine oxide
diethyldodecylamine oxide
diethyltetradecylamine oxide
dipropyldodecylamine oxide
bis-(2-hydroxyethyl)dodecylamine oxide
bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropyl
amine oxide
(2-hydroxypropyl)methyltetradecylamine oxide
dimethylolethylamine oxide
dimethyl-(2-hydroxydodecyl)amine oxide

and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds.

(6) A detergent having the formula $R^1R^2R^3P \rightarrow O$ (phosphine oxide detergent) wherein R^1 is an alkyl group containing from about 10 to about 28 carbon atoms, from 0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of R^1 which is an alkyl group containing from about 10 to about 18 carbon atoms and 0 ether linkages, and each of R^2 and R^3 are selected from the group consisting of alkyl radicals and hydroxyalkyl radicals containing from 1 to about 3 carbon atoms.

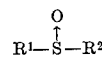
12

Specific examples of the phosphine oxide detergents include:

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

and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds.

(7) A detergent having the formula:

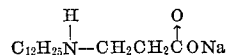


(sulfoxide detergent) wherein R^1 is an alkyl radical containing from about 10 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxyl substituents at least one moiety of R^1 being an alkyl radical containing 0 ether linkages and containing from about 10 to about 18 carbon atoms, and wherein R^2 is an alkyl radical containing from 1 to 3 carbon atoms and from one to two hydroxyl groups:

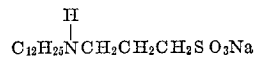
octadecyl methyl sulfoxide
dodecyl methyl sulfoxide
tetradecyl methyl sulfoxide
3-hydroxytridecyl methyl sulfoxide
3-methoxytridecyl methyl sulfoxide
3-hydroxy-4-dodecoxybutyl methyl sulfoxide
octadecyl 2-hydroxyethyl sulfoxide
dodecylethyl sulfoxide

(C) Ampholytic synthetic detergents

Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines, 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 at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are sodium 3-(dodecylamino)-propionate:



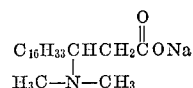
sodium 3-(dodecylamino)propane-1-sulfonate:



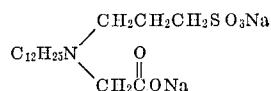
sodium 2-(dodecylamino)ethyl sulfate:



sodium 2-(dimethylamino)octadecanoate:

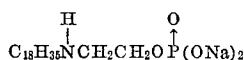


disodium 3-(N-carboxymethyl-dodecylamino)propane-1-sulfonate:

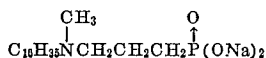


13

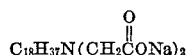
disodium 2-(oleylamino)ethyl phosphate:



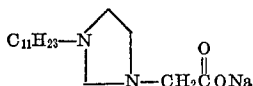
disodium 3-(N-methyl-hexadecylamino)propyl-1-phosphonate:



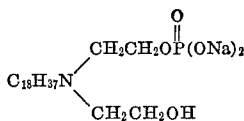
disodium octadecyl-iminodiacetate:



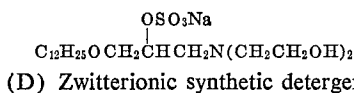
sodium 1-carboxymethyl-2-undecyl-imidazole:



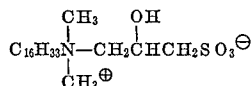
disodium 2-[N-(2-hydroxyethyl)octadecylamino] ethyl phosphate:



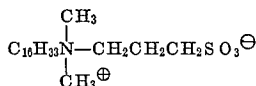
and sodium N,N-bis-(2 - hydroxyethyl) - 2 - sulfate-3-dodecoxypropylamine:



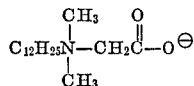
Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium and phosphonium or tertiary sulfonium compounds, in which the cationic atom may be part of a heterocyclic ring, and in which the aliphatic radical may be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms, and at least one aliphatic substituent contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are 3 - (N,N - dimethyl - N-hexadecyl-ammonio)-2-hydroxypropane-1-sulfonate:



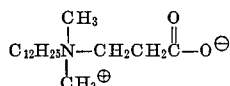
3-(N,N - dimethyl - N - hexadecylammonio)propane-1-sulfonate:



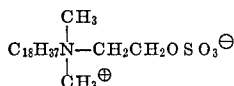
2-(N,N-dimethyl-N-dodecylammonio)acetate:



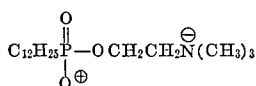
3-(N,N-dimethyl N-dodecylammonio)propionate:



2-(N,N-dimethyl-N-octadecylammonio)-ethyl sulfate:

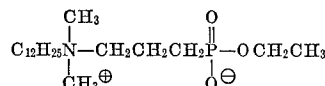


2-(trimethylammonio)ethyl dodecyl-phosphonate:

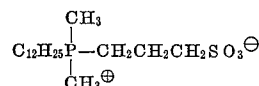


14

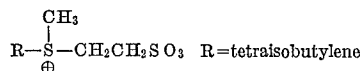
ethyl 3-(N,N-dimethyl - N - dodecylammonio)-propyl-phosphonate:



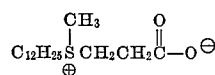
3-(P,P-dimethyl - P - dodecylphosphonio) - propane-1-sulfonate:



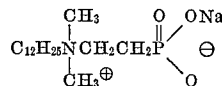
2-(S-methyl - S - tert.-hexadecyl-sulfonio)ethane-1-sulfonate:



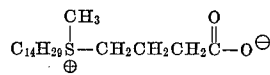
3-(S-methyl-S-dodecylsulfonio)-propionate:



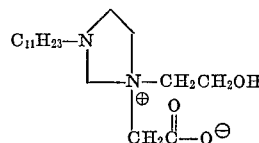
sodium 2-(N,N - dimethyl - N - dodecylammonio)ethyl phosphonate:



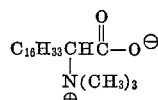
30 4-(S-methyl-S-tetradecylsulfonio) butyrate:



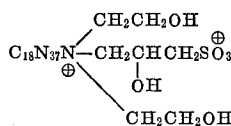
35 1-(2-hydroxyethyl)-2-undecyl-imidazolium-1-acetate:



2-(trimethylammonio)-octadecanoate:



50 and 3-(N,N-bis - (2 - hydroxyethyl) - N - octodecylammonio)-2-hydroxypropane-1-sulfonate:



Some of these detergents are described in the following U.S. Pats. 2,129,264; 2,178,353; 2,774,786; 2,813,898; and 2,828,332.

A detergent composition prepared according to the present invention contains as essential ingredients (a) a detergent ingredient and (b) a builder ingredient. In simplest terms, a composition can contain a single detergent compound and a single builder compound. On the other hand, it frequently is desirable to formulate a detergent composition in which the detergent ingredient consists of mixtures of detergent compounds selected from the foregoing classes. Thus, for example, the active ingredient can consist of a mixture of two or more anionic detergents; or a mixture of an anionic detergent and a nonionic detergent; or, by way of another example, the active detergent can be a ternary mixture of two anionic detergents and a Zwitterionic detergent.

The part of the complete formulation that functions as a builder can likewise be composed of a mixture of builder compounds. For example, the builder compounds described herein can be mixed together with other water-soluble inorganic alkaline builder salts such as sodium tripolyphosphate or potassium pyrophosphate or potassium pyrophosphates or a water-soluble organic builder salt such as water-soluble salts of nitrilotriacetic acid, ethylenediaminetetraacetic acid, ethane-1-hydroxy-1,1-diphosphonic acid. Still further, the builder component of a complete formulation can consist of ternary mixtures of these several types of builder compounds.

Water-soluble inorganic alkaline builder salts which can be used in this invention in combination with the novel carboxy-phosphonate compounds described herein are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates. Ammonium and substituted ammonium salts of these materials can also be used. Specific examples of suitable salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium and potassium pyrophosphate, sodium and ammonium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium orthophosphate and potassium bicarbonate.

Examples of suitable organic water-soluble organic alkaline sequestrant builder salts which can be used mixed with the carboxy-phosphonate compounds of this invention are alkali metal (sodium, potassium, lithium), ammonium or substituted ammonium, aminopolycarboxylates, e.g., the above mentioned sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylenediaminetriacetates, sodium and potassium nitrilotriacetates and sodium, potassium and triethanolammonium N-(2-hydroxyethyl)-nitrilotriacetates. The alkali metal salts of phytic acid, e.g., sodium phytate, are also suitable as organic alkaline sequestrant builder salts. Certain other organic builders which can be used are water-soluble salts of ethane-1-hydroxy-1,1-diphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, methylene diphosphonic acid, and the like.

The builder mixtures taught herein are highly effective and, in general, can be used to permit the attainment of equal detergency with a smaller total quantity of builder in relation to the total quantity of active detergent ingredient.

The built detergent compositions of the present invention can be formulated and prepared into any of the several commercially desirable solid and liquid forms including, for example, granules, flakes, tablets, and water-based and alcohol-based liquid detergents, and the like. According to one embodiment of the present invention, solid detergent compositions are prepared containing a detergent (sole active or a mixture of detergents) and a builder (single compound or a mixture) in the by weight ratio (detergent to builder) of about 2:1 to about 1:10, and preferably from about 1:1 to about 1:6. A special embodiment of this invention is a built liquid detergent composition containing a detergent and a builder in the by weight ratio (detergent to builder) of 3:1 to about 1:10; preferably 2:1 to about 1:3. Potassium salts are especially useful in liquid formulations due to the increased solubility characteristics of potassium over sodium.

Built liquid detergents are usually water based or have a mixture of water and alcohol in the liquid vehicle. Such liquid vehicles can be satisfactorily employed in formulating a composition according to the present invention. Accordingly, a sample built liquid detergent composition of this invention can consist essentially of a detergent ingredient (a single detergent or a mixture of detergents) and a builder (either as a single builder or in admixture with other builders), with the balance of the composition to 100% being a liquid vehicle such as water or a water-alcohol mixture, and the like.

The built detergent compositions of the present inven-

tion perform at their maximum level in a washing solution which has a pH in the range of from about 8 to about 12. Within this broad range, it is preferred to operate at a pH of from about 9.5 to 11. The detergent and the builder can be neutralized to a degree sufficient to insure that this pH prevails in any washing solution. If desired, other alkaline materials can be added to the complete formulation to provide for any pH adjustments desired. A preferred embodiment is to have the detergent composition whether in solid or liquid form provide a pH in the aforementioned ranges at the usual recommended usage levels.

In a finished detergent formulation, there can be present other materials which make the product more effective or more aesthetically attractive. The following are mentioned only by way of example. A water-soluble sodium carboxymethyl cellulose can be added in minor amounts to inhibit soil redeposition. Tarnish inhibitors such as benzotriazole or ethylenethiourea can also be added in amounts up to about 3%. Fluorescers, and brighteners, enzymes, perfumes, coloring agents, while not per se essential in the compositions of this invention, can be added in minor amounts. As already mentioned, an alkaline material or alkali such as sodium or potassium hydroxide can be added as supplementary pH adjusters. Other usual additives include sodium sulfate, sodium carbonate, water, and the like. Corrosion inhibitors are also frequently used. Water-soluble silicates are highly effective corrosion inhibitors and can be added if desired at levels of from about 3% to about 8% by weight of the total composition. Alkali metal, preferably potassium and sodium silicates, are preferred having a weight ratio of $\text{SiO}_2:\text{M}_2\text{O}$ of from about 1.0:1 to 2.8:1. (M refers to sodium or potassium.) Sodium silicate having a ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of from about 1.6:1 to 2.45:1 is especially preferred.

In the embodiment of this invention which provides for a built liquid detergent, a hydrotrope is desirable. Suitable hydrotropes are water-soluble alkali metal salts of toluenesulfonate, benzenesulfonate, and xylenesulfonate. Preferred hydrotropes are potassium or sodium toluenesulfonates. The hydrotrope salt may be added at levels up 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 function as a solubilizing agent and 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, the invention. Each of the compositions in the following examples give in solution a pH within the desired range of from about 8 to about 12.

EXAMPLE A

A granular built detergent composition according to this invention has the following formulation:

	Percent
Sodium alkyl benzene sulfonate in which the alkyl is a straight chain dodecyl radical	18
Hexasodium ethane-1,2-dicarboxy-1,2-diphosphonate	50
Sodium sulfate	15
Sodium silicate (ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of 2:1)	7
Water	10

This heavily built detergent composition is especially valuable for laundering heavily soiled clothes.

The straight chain dodecyl benzene sodium sulfonate in the preceding composition can be replaced on an equal weight basis by either branched chain dodecyl benzene sodium sulfonate, sodium tallow alkyl sulfate, sodium coconut oil alkyl sulfate, sodium olefin sulfonate as described in the specification derived from alpha olefins having an average of 14 carbon atoms in the molecule, or a mixture of straight chain dodecyl benzene sodium sul-

fonate and sodium tallow alkyl sulfate on an equal weight basis. The hexasodium builder salt can be replaced by an ammonium, potassium, or lithium salt; hexasodium salt of ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonate; a 1:1 mixture of sodium tripolyphosphate and hexasodium ethane-1,2-dicarboxy-1,2-diphosphonate; a 1:1:1 ternary mixture of sodium tripolyphosphate, sodium nitrilotriacetate and hexasodium ethane-1,2-dicarboxy-1,2-diphosphonate; tetrasodium ethene-1,2-dicarboxy-1-phosphonate; or tetrasodium dimethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate.

EXAMPLE B

Another effective granular detergent composition has the following formulation:

	Percent
Straight chain dodecyl benzene sodium sulfonate (anionic detergent) -----	4
Sodium tallow alkyl sulfate (anionic detergent) ----	4
Dodecyl methyl sulfoxide -----	2
Hydrogenated marine oil fatty acid -----	2
Tetrasodium ethene-1,2-dicarboxy-1-phosphonate----	60
Sodium silicate (ratio of SiO ₂ :Na ₂ O of 1.6:1) -----	10
Sodium sulfate -----	14
Water -----	6

In this example, the total active detergent of 10% can be totally the nonionic species. In addition, the 2% dodecyl methyl sulfoxide can be replaced by the product of a condensation reaction between dodecyl phenol and 5 moles of ethylene oxide per mole of dodecyl phenol, or by 3 - (dodecyldimethylammonio)-2-hydroxy propane-1-sulfonate.

The tetrasodium salt of the builder can be added as the salt or it can be present as the free acid neutralized in situ to any salt form ranging from the monosodium or monopotassium salt to the fully neutralized tetrasodium or tetrapotassium salt. The builder can be replaced with an equal weight of sodium-1,2-dihydroxy-1-hydroxy-1,2 - diphosphonate, or potassium - 1,2 - dicarboxy-2-hydroxy-1,2-diphosphonate, or a 1:1 mixture of these two builders.

EXAMPLE C

Another example of a granular detergent composition of outstanding efficiency:

	Percent
Straight chain tridecylbenzene sodium sulfonate ¹ (anionic detergent) -----	20
Trisodium ethane - 1,2-dicarboxy-1,2-diphosphonate--	49
Sodium silicate (ratio SiO ₂ :Na ₂ O of 2:1) -----	6
Sodium sulfate -----	14
Water -----	11

¹This detergent compound is also referred to as linear tridecyl benzene sodium sulfonate.

In this example, the anionic detergent can be replaced on an equal weight percentage with an olefin sodium sulfonate in which the olefin sulfonate consists of a mixture of chain lengths ranging from 10 to about 18 carbon atoms. The dicarboxy diphosphonate builder can be replaced on an equal weight with sodium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonate, potassium ethene-1,2-dicarboxy-1-phosphonate, or diethyl ethane-1,2-dicarboxy-1,2-diphosphonate.

EXAMPLE D

The following detergent composition provides satisfactory cleaning results:

	Percent
Dodecyldimethylamine oxide (nonionic detergent) -	16.0
Dimethyl (P,P')ethane - 1,2 - dicarboxy - 1,2 - diphosphonic acid -----	40.0
Toluene sulfonate-----	1.8

	Percent
Sodium silicate (ratio of SiO ₂ :Na ₂ O of 2:1)-----	8.0
Sodium sulfate-----	2.0
5 Diethanolamide of coconut fatty acid-----	1.9
Benzotriazole -----	.02
Balance to 100%, water.	

In this composition, the nonionic detergent can be replaced by tetradecyl dimethyl phosphine oxide, sodium-3-dodecylaminopropionate, sodium - 3 - dodecylaminopropanesulfonate, 3(N,N - dimethyl-N-hexadecylammonio)-propane-1-sulfonate or 3-(N,N-dimethyl-N-dodecylammonio)-2-hydroxypropane-1-sulfonate. Twenty percent of the builder can be replaced with an equal weight replacement of trisodium ethane-1-hydroxy-1,1-diphosphonate,

As mentioned above, one of the desirable attributes of a satisfactory builder compound is the ability to sequester or complex hardness minerals which may be present in a washing solution. The builder compounds of the present invention have satisfactory sequestering properties. The preferred compounds of the present invention, i.e., those builders falling within groups A and B above, are especially noteworthy in this respect. The test used to demonstrate the sequestering properties is referred to as a Swatch-Dip test and is described below.

This test measures the relative sequestering ability of a compound by employing a fabric-swatch impregnated with soap and an aqueous solution containing a predetermined level of calcium hardness minerals. Briefly, the procedure calls for preparing an aqueous solution containing the hardness ions and dipping or immersing into the solution a fabric-swatch which has been impregnated with a measured amount of soap. The swatch remains in the solution for a predetermined amount of time. A measurement is then made to determine the amount of free calcium which has been adsorbed by the fabric-swatch. The identical procedure is then repeated but with a predetermined concentration of a sequestant compound added to the aqueous solution containing the calcium ions. Measurements of adsorbed calcium are again made and comparisons drawn. Differences between the amounts of calcium adsorbed in tests with an without sequestrants are attributed to the ability of the sequestant to sequester the calcium and thereby decrease the level of free calcium ion concentration available for adsorption by the immersed fabric-swatch. A percentage is obtained in this manner which is referred to as "percentage hardness retained by sequestant."

This procedure was conducted with representative compounds of the present invention as well as sodium tripolyphosphate and sodium ethylenediaminetetraacetate. Sodium tripolyphosphate contains three phosphorus atoms; ethylenediaminetetraacetate contains four carboxylate groups. The representative compounds of this invention selected for this comparison were the following: sodium ethane-1,2-dicarboxy-1,2-diphosphonate (EDCDP); sodium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonate (EDCDHDP); sodium ethene-1,2-dicarboxy-1-phosphonate (EDCP); and dimethyl(P,P')ethane-1,2-dicarboxy-1,2-diphosphonate (Me₂EDCDP).

The results obtained by this procedure are presented in FIG. I. An examination of this drawing indicates that ethane-1,2-dicarboxy-1,2-diphosphonate (EDCDP) and ethane - 1,2 - dicarboxy-1,2-dihydroxy-1,2-diphosphonate (EDCDHDP) achieved higher values than sodium tripolyphosphate at a builder concentration as sodium salt of 0.03% to 0.06%. In addition, ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonate and ethene dicarboxy monophosphonate scored higher at a concentration of 0.01% over that obtained by sodium tripolyphosphate. Moreover, as regards ethylenediaminetetraacetate (EDTA) it will be seen that the lines for ethane-1,2-dicarboxy-1,2-dihydroxy-1,2 - diphosphonate, ethane-1,2-dicarboxy-1,2-diphospho-

nate, and ethene-1,2-dicarboxy-1-monophosphonate are all considerably steeper up to a concentration of 0.03% than that for ethylenediaminetetraacetate (EDTA) indicating better sequestering performance. The improved efficiency demonstrated by these curves for representative builders of the present invention is self-evident. The only representative compound of the present invention whose sequestering results appear to be significant but inferior to sodium tripolyphosphate and ethylenediaminetetraacetate is dimethoxy(P,P')ethane - 1,2-dicarboxy-1,2-diphosphonate (Me₂EDCDP). It is apparent, however, that even this latter compound has substantial sequestering properties as evidenced by a comparison between the curves for this compound and ethylenediaminetetraacetate at a concentration range of 0.01% up to 0.03%.

The efficiency advantage which the builder compounds of the present invention provide over a standard commercially used builder such as sodium tripolyphosphate is demonstrated by the following evaluation.

A detergency test was conducted which is referred to as a facial swatch test. This test involves a procedure of soiling a cloth swatch with natural soil by attaching a swatch (about 5 inches by 5 inches) to the plunger cup of an electric vibrator massager. Two swatches are soiled from an individual subject by massaging the right and left halves of the face respectively for one minute each. The soiled swatches are then randomized into groups to statistically provide equal numbers of left and right samples. The swatches are then washed, rinsed and graded and the cycle is repeated nine times. The washing step consists of laundering the soiled swatches in an aqueous solution having a temperature of 140° F., a pH of 10, and containing 7 grains hardness.

A mechanical washer is used which is equipped with an agitator and otherwise simulates an ordinary home washing machine. The detergent compositions tested consisted of a detergent at a concentration of .03% in the wash water and a builder at a concentration of .03% and .06%. The compounds representative of the present invention which were used as comparisons with sodium tripolyphosphate were: sodium ethane-1,2-dicarboxy-1,2-diphosphonate (EDCDP); sodium ethane-1,2-dicarboxy-1,2-dihydroxy - 1,2 - diphosphonate (EDCDHDP) and sodium ethene-1,2-dicarboxy-1-phosphonate (EDCP).

Following the washing of the soiled swatches, they were rinsed and dried and then whiteness measurements were made with a commercially available photoelectric reflectometer, i.e., a Hunter Color and Color Difference Meter manufactured by Henry A. Gardner Laboratory, Inc. This instrument is designed to distinguish color differences and operates on the tristimulus colorimeter principle. According to this principle, a 45 degree 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 (TiO₂ being taken as a standard white) of the test specimen is calculated by introducing the lightness and chromaticity values so obtained into a complex formula supplied by the manufacturer. An evaluation of relative whiteness performance compared to a standard detergent composition is thus obtained for the test formulations. A more comprehensive description of this device and its mode of operation appears in *Color In Business, Science and Industry* by Deane B. Judd, pages 260-262; published by John Wiley & Sons, New York (1952).

The measurements obtained by the foregoing procedure are given below in the table. The efficiency advantage becomes readily apparent from a consideration of these figures.

The synthetic detergent which was used in each of the following evaluations at a concentration in the wash solutions of .03% was sodium dodecylbenzene sulfonate, the dodecyl group being derived from tetrapropylene.

TABLE

Builder compound	Column I	Column II
	.03%	.06%
1. Sodium ethane-1,2-dicarboxy-1,2-diphosphonate	90.79	90.97
2. Sodium ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonate	90.72	
3. Sodium ethene-1,2-dicarboxy-1-phosphonate	87.78	
4. Sodium tripolyphosphate	88.3	90.74

In the foregoing table a statistically significant difference is .68.

It can be seen from Column II that at a concentration of .06% the value given for sodium ethane-1,2-dicarboxy-1,2-diphosphonate of 90.97 is substantially the same as, although just slightly greater than, the value for sodium tripolyphosphate which is 90.74. More notable, however, is the fact that the performance obtained with ethane-1,2-dicarboxy - 1,2 - diphosphonate and ethane - 1,2 - dicarboxy - 1,2 - dihydroxy - 1,2 - diphosphonate at concentrations of .03% are also substantially equivalent to the performance of sodium tripolyphosphate at double the concentration or .06%. This indicates that these two representative compounds of the present invention can be used at only half the concentration of sodium tripolyphosphate without sacrificing cleaning performance. The performance of sodium tripolyphosphate at .03% as noted in the table was 88.3. This value is substantially less, and significantly so, from the performance of ethane-1,2-dicarboxy - 1,2 - diphosphonate and ethane - 1,2 - dicarboxy - 1,2 - dihydroxy - 1,2 - diphosphonate at an equal concentration. Of the compounds of the present invention, only ethene-1,2-dicarboxy-1-phosphonate scored less than sodium tripolyphosphate and this was not statistically significant as measured by the yardstick of .68.

In addition to the preceding performance evaluations, another demonstration involves measuring cleaning, whiteness and whiteness maintenance properties. For purposes of this invention, these terms have the following meanings. The term "cleaning" identifies the ability of a detergent composition to remove soil from soiled fabrics. In part, this applies to the removal of deeply embedded soil deposits such as occurs, for instance, at the collars and cuffs of shirts and blouses. Whiteness is a more general term which identifies or represents a measurement of the ability of a built detergent composition to whiten areas which are only slightly or moderately soiled. Whiteness maintenance is a term which is used to measure the ability of a detergent formulation to prevent the soil which has been removed during a normal washing cycle from being redeposited upon the fabrics during the laundering process, e.g., during washing and rinsing steps, etc.

These demonstrations were made by washing naturally soiled white dress shirts with detergent compositions built with different builder materials. Shirts with detachable collars and cuffs were worn by male subjects under ordinary conditions for a certain period of time. The collars and cuffs were then detached and washed in an ordinary agitator type washing machine using solutions of the built detergent compositions being evaluated.

For this demonstration, sodium ethane-1,2-dicarboxy-1,2-diphosphonate (EDCDP) and sodium ethene-1,2-dicarboxyl-1-phosphonate (EDCP) were used as representative builder compounds coming within the scope of the present invention.

The demonstration employs a detergent composition consisting only of a detergent and a builder compound. This is done in order to obtain as accurate a measurement as possible of the builder property of each of the sample compounds. None of the usual additives such as sulfates, silicates, fluorescers, anti-redeposition agents, etc., are used in these tests. By limiting the compositions to only two ingredients, i.e., a detergent and a builder, there can be no interference or masking of the effectiveness of the builders. The concentration of the detergent in the wash-

ing solution was .03% by weight. The concentration of the builders in the washing solution varied and included concentrations of .03%, .045% (STP only), and .06%. These percentages correspond to concentrations of .03, .045 and .06 gram per 100 ml. of water. In addition, the wash solutions containing 7 grains per gallon hardness (equivalent CaCO_3) were adjusted with sodium hydroxide to a pH of 10. The temperature of the washing solution was 140° F. The duration of the washing cycle was 10 minutes.

The washed and dried collars and cuffs were graded by means of a visual comparison with other collars and cuffs which had been similarly worn and soiled but which were washed with a standard built detergent composition. The visual comparisons were made by a trained panel of five people who were unfamiliar with any specific details and objectives of the tests. Their judgments were made independently.

Their visual judgments were expressed on a scale ranging from zero to ten. This records the relative cleaning performance grades among the several compositions being evaluated. Zero on the cleaning grade scale represents a cleaning level obtained by washing with water alone, i.e., employing no detergent formulation. A value of ten represents the cleaning level of a specially formulated standardized detergent composition under optimum conditions. For purposes of this evaluation, a value grade of five represents a level of cleaning that is considered satisfactory in household practice.

The results obtained with these representative materials are presented along with results obtained with sodium tripolyphosphate (STP) in FIG. II.

In FIG. II, a difference in the cleaning grading scale of 1 unit represents a significant difference. By this is meant that a housewife could readily and consistently see a significant cleaning difference between two fabrics which have scores separated by a magnitude of at least 1 unit.

From FIG. II, Part A, it will be seen that the concentration of .03% EDCDP offers substantial improvements in cleaning. STP performed at a value of 1.4 on the Performance Scale whereas EDCDP performed at a value of 4.7 which is at least three times better than the STP value. As a matter of fact, from Part A of FIG. II it is apparent that the cleaning results obtained with EDCDP at a concentration of .03% is substantially equivalent to the cleaning grade obtained with STP at .06% concentration. The efficiency advantage of this latter comparison in favor of the compound representative of the present invention is readily apparent. Moreover, it is noted that at a concentration of .06% EDCDP received a performance grade of 6.5 as compared to STP of 5.0.

The collar and cuff samples washed in accordance with the preceding discussion and for which cleaning results are presented in Part A of FIG. II were thereafter examined for whiteness performance results.

The whiteness performance grades are presented in FIG. II, Part B. The superior results obtained with EDCDP are readily apparent. Performance grades for STP at a concentration of .045 and .06% failed to equal the excellent results obtained with EDCDP.

The evaluation of "whiteness maintenance" capability of the respective builders was performed by the following method. Unsoiled swatches of cotton terry cloth were washed with the wash solutions obtained from the cleaning tests. In other words, unsoiled swatches are added to the "dirty" wash water from the "cleaning" tests. The swatches are dried and then the whiteness thereof is measured by a Hunter Color and Color Difference Meter following the same procedure described above. The soil adhering to the swatches is a relative measure of soil which has been adsorbed from the washing solutions containing the aforementioned representative builders. Although factors are involved here other than the anti-redeposition characteristics of the built detergent composition, it is still an effective way of measuring and

demonstrating this property. For showing relative performance, the test is especially valuable.

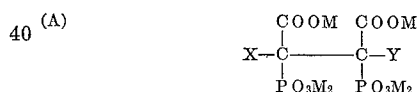
The results obtained by this procedure are presented in FIG. II-C. By virtue of this test, it was ascertained that the representative compound of the present invention has valuable whiteness maintenance properties. STP was evaluated at only one concentration, namely, .06%, and received a performance grade of 5.0. This same result was achieved by EDCDP at a concentration of only .03% which was exactly one-half of the amount of STP required to attain that performance grade. At equal concentrations of .06%, EDCDP received a performance grade of two full units higher than STP, that is, 7 vs. 5.

In each of the preceding tests where gradings were made for cleaning, whiteness and whiteness maintenance, EDCDP was evaluated only at a concentration of 0.03%. It was somewhat less effective than STP in the cleaning evaluation. However, in the other two evaluations, EDCDP surpassed STP. For instance, in the whiteness evaluation EDCDP received a performance grade of 5.7. This is somewhat less than EDCDP but substantially better than the values obtained by STP. Likewise, and quite surprisingly, in the area of whiteness maintenance, EDCDP evaluated at a concentration of .03% received a higher score than both EDCDP and STP (0.6%).

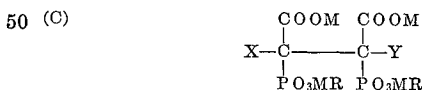
The foregoing description of the present invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of this invention.

What is claimed is:

1. A detergent composition consisting essentially of a water soluble organic synthetic detergent selected from the group consisting of anionic, nonionic, ampholytic, and zwitterionic detergents and mixtures thereof and a detergency builder selected from the group consisting of



and

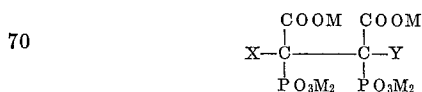


in which M is hydrogen, alkali metal or ammonium, and R is an alkyl group having 1 to about 6 carbon atoms, and X and Y are each hydrogen or hydroxy wherein said detergent and said builder are in a ratio by weight of from about 5:1 to about 1:20.

2. A detergent composition according to claim 1 in which said detergent and said builder are in a ratio by weight of 2:1 to about 1:10.

3. A detergent composition according to claim 1 in which the organic synthetic detergent is an anionic detergent.

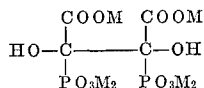
4. A detergent composition according to claim 1 in which said builder is a compound having a formula:



in which M is hydrogen or alkali metal, and X and Y are each hydrogen or hydroxy.

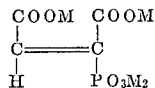
23

5. A built detergent composition according to claim 1 in which said builder is a compound having a formula:



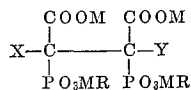
in which M is hydrogen or alkali metal.

6. A built detergent composition according to claim 1 in which said builder is a compound having a formula:



in which M is hydrogen or alkali metal.

7. A built detergent composition according to claim 1 in which said builder is a compound having a formula:



in which M is hydrogen or alkali metal, and R is an alkyl

24

group having 1 to about 6 carbon atoms, and X and Y are each hydrogen or hydroxy.

8. A detergent composition according to claim 1 in which said builder is an alkali metal salt of ethane-1,2-dicarboxy-1,2-diphosphonic acid.

5 9. A detergent composition according to claim 1 in which said builder is an alkali metal salt of ethane-1,2-dicarboxy-1,2-dihydroxy-1,2-diphosphonic acid.

References Cited

- 10 J. Org. Chem., vol. 30, pp. 2829-2830.
J. Agr. Food Chem., vol. 15, pp. 940-2.

15 LEON D. ROSDOL, Primary Examiner

M. HALPERN, Assistant Examiner

U.S. Cl. X.R.

20 252-87, 137, 161; 260-932, 942