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(54) **Low phosphate detergent composition for fabric washing.**

(57) A detergent composition having a phosphorous content of no more than 6 % and a solution pH of less than 10 contains an organic detergent, a carboxylate builder having a pK_a of less than 9 and a small amount of a polyphosphonic acid. Typical compositions utilise a citrate or succinate builder together with ethylene diaminetetramethylene phosphonate. The compositions are particularly effective in the area of bleachable stain removal.

EP 0 001 310 A1

Low-Phosphate Detergent Composition
for Fabric Washing

The present invention relates to detergent compositions and in particular to built detergent compositions adapted for fabric washing.

Compositions comprising a detergent and a builder compound are generally referred to in the art as "built" detergent compositions. When a large portion of the detergency builder is used in relation to the detergent, the compositions are characterized as "heavy duty" compositions intended primarily for laundering heavily soiled fabrics. Detergent compositions containing lower proportions of builder are "light-duty" compositions intended for lightly soiled fabrics, "fine" fabrics and woollens.

The use of detergency builders as adjuncts with organic water-soluble synthetic detergents and the property which said materials have for improving the over-all detergency performance of such detergents are well-known. A variety of such materials, especially the sodium polyphosphates, are well-known for this detergency builder use. However, some concern has been expressed that certain algae in bodies of water resort to phosphorus-containing materials for nutritional value. Phosphorus-free builder compounds would be free of such criticism. Therefore, a need has been created for detergency builders which are biodegradable but which are comparable to sodium tripolyphosphates in builder effectiveness.

The mechanism whereby detergency builders function to improve the detergency action of water-soluble organic detergent compounds is not precisely known, but appears to be some combination of such factors as water-softening action soil suspension and anti-redeposition effects and pH adjustment. However, present theory does not allow the prediction of which compounds will serve as effective detergency builders. Accordingly, it has been empirically discovered that a variety of materials, including the aforementioned tripolyphosphates, as well as phosphonates, nitrilotriacetates, sodium sulphate and various silicates and aluminosilicates, all serve as

detergency builders, at least to some extent.

5 A variety of polycarboxylates have been previously disclosed to be useful as detergency builders, water softeners and curd dispersants in detergent compositions. For example, U.S. Patent 2,264,103, relates to the use of various poly-
10 carboxylic acids as detergency builders and water softeners. This patent teaches that polycarboxylates having three or more carboxyl groups per molecule are useful as detergency builders and water softeners. Netherlands Application
15 6,501,871, relates to the use of various polymers, such as those of itaconic and aconitic acids, in laundry detergents. British Patent 1,261,829 discloses the use of oxydisuccinic acid as a detergency builder while British Patent 1,379,241 discloses the use of carboxymethyloxy succinic acid as a
20 detergency builder. It may therefore be seen that a variety of poly-carboxylates have been heretofore suggested for use as detergency builders. However, these materials suffer from a variety of defects and have not found general acceptance for this use. For example, many such materials are
25 difficult and expensive to prepare or have to be used in substantial quantities in order to secure effective building capacity. When, on the other hand, the content of polycarboxylate builder is reduced to an economically viable level, the resulting compositions are frequently found to be defective in some aspect of builder performance such as calcium sequestration or pH buffering; in other words they behave as typical "under-built" compositions.

Another consideration in the use of polycarboxylates as builders is that certain of the most common and cheapest
30 materials have their greatest buffering effectiveness at relatively low pH levels where conventional bleaching agents such as perborates and percarbonates are themselves least effective. To a certain extent, therefore, these polycarboxylates and bleaching agents are mutually incompatible
35 and the resulting compositions are consequently found to be deficient in the area of bleachable stain removal performance.

A further aspect of bleach/polycarboxylate incompatibility is that hydroxycarboxylates such as citric acid are
40 known to decompose at higher wash temperatures and can therefore only be used effectively in relatively low temperature washing processes. Perborate and percarbonate, on the other hand, are ineffective at low temperatures in the

absence of bleach activators. Once again, therefore, either building or bleaching performance must, to a certain extent, be compromised when using hydroxycarboxylates as builders

5 The present invention therefore provides low or zero phosphate containing detergent compositions having substantially equivalent cleaning performance to a conventional tripolyphosphate-built composition. The invention also provides compositions having effective detergency and building performance based on lower than conventional levels of certain polycarboxylate builders. The invention further provides 10 polycarboxylate-built detergent compositions having improved cleaning performance in the area of bleachable stain detergency.

15 According to the present invention, there is provided a detergent composition having a phosphorus content of no more than 6%, preferably no more than 5%, and a pH in 1% aqueous solution of less than 10, which comprises

- 20 (a) from 2 to 75% of an organic detergent selected from anionic, nonionic, amphoteric and zwitterionic detergents and mixtures thereof,
- (b) from 4 to 50% of a carboxylate or polycarboxylate having a first carboxyl logarithmic acidity constant (pK_1) of less than 9, and
- 25 (c) from 0.01 to 4% of a polyphosphonic acid or salt thereof.

30 Preferably, the detergent compositions of the invention have a pH in 1% aqueous solution of less than about 9.5, and more preferably have a pH in the range from about 6 to about 9.0, especially from about 7 to about 8.5. In preferred embodiments, the carboxylate or polycarboxylate builder has a logarithmic acidity constant in the range from about 2 to about 8.5, especially from about 4 to about 7.5, and has a logarithmic calcium stability constant ($pK_{Ca^{++}}$) in the range from about 2 to about 7. Preferred compositions contain from 35 about 8 to about 30% by weight of the carboxylate or polycarboxylate builder, especially from about 12 to about 25% by weight, and from about 0.2 to about 3.5% by weight of the polyphosphonate, especially about 0.5 to 2.2% by weight.

40 The various essential and optional components of the instant compositions will now be described.

Organic Detergent

The detergent active component of the present compositions can be anionic, nonionic, ampholytic or zwitterionic in nature

or can be mixtures thereof.

The detergent compositions of the invention contain the active system in an amount of from about 2% to about 75% by weight. For solid granular compositions, the active systems is generally in the range from about 4% to about 30%, more preferably from about 6% to about 15% of the compositions. In liquid compositions, higher active contents, for example about 20% to about 70% are normally employed. A typical-listing of anionic, nonionic, zwitterionic and amphoteric surfactants useful herein appears in USP 3,925,678 incorporated herein by reference. The following list of detergent compounds which can be used in the instant compositions is representative of such materials.

Water-soluble salts of the higher fatty acids, i.e. "soaps", are useful as the anionic detergent component of the compositions herein. This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Soaps can be made by direct saponification of fats and soils or by the neutralization of free fatty acids. 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.

A highly preferred class of anionic detergents includes water-soluble salts, particularly the alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22, especially from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic detergents which form part of the detergent compositions of the present invention are the sodium and 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; and sodium and 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, eg. those of the type described in USP 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl group is about 11.8 carbon atoms,

abbreviated as C_{11.8} LAS.

5 A preferred alkyl ether sulfate surfactant component of the present invention is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of about 12 to 16 carbon atoms, preferably from about 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from about 1 to 4 mols of ethylene oxide.

10 Other anionic detergent compounds herein include the 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; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing about 1 to about 10
15 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts of esters of α -sulfonated fatty acids containing from about 6 to 20 carbon atoms in
20 the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from
25 about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; water-soluble salts of paraffin sulfonates containing from about 8 to 24, especially 14 to 18 carbon atoms, and β -alkyloxy
30 alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Anionic surfactant mixtures can also be employed, for example 5:1 to 1:5 mixtures of an alkyl benzene sulfonate
35 having from 9 to 15 carbon atoms in the alkyl radical and mixtures thereof, the cation being an alkali metal preferably sodium; and from about 2% to about 15% by weight of an alkyl ethoxy sulfate having from 10 to 20 carbon atoms in the alkyl radical and from 1 to 30 ethoxy groups and mixtures thereof,
40 having an alkali metal cation, preferably sodium.

Water-soluble nonionic synthetic detergents are also useful as the detergent component of the instant composition.

Such nonionic detergent materials can 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 polyoxyalkylene group 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.

Examples of suitable nonionic detergents include:

1. The polyethylene oxide condensates of alkyl phenol, eg. the condensation products of alkyl phenols having an alkyl group containing from 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, for example, from polymerised propylene, di-isobutylene, octene and nonene. 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; nonylphenol condensed with 20 moles of ethylene oxide per mole of nonylphenol and di-iso-octylphenol condensed with 15 moles of ethylene oxide.
2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 1 to about 30 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 12, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty and greasy soils, and in the presence of hardness sensitive anionic surfactants such as alkyl benzene sulphonates. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats of prepared by the Ziegler process from ethylene, eg. myristyl, cetyl, stearyl alcohols), or partly branched such as the Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol and Neodol being Trade Names of Shell) or Synperonics, which are understood to have about 50% 2-methyl branching (Synperionic is a trade name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the

Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-11, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 14.

5 the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol
10 per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 16 carbon atoms in the alkyl group and up
15 to about 11, especially from about 3 to 9, ethoxy residues per molecule.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the
20 hydrophobic portion generally falls in the range of about 1500 to 1800. Such synthetic nonionic detergents are available on the market under the trade name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

Semi-polar nonionic detergents include water-soluble
25 amine oxides containing one alkyl moiety of from about 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxide detergents containing one alkyl moiety of about 10 to 28 carbon
30 atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxide detergents containing one alkyl moiety of from about 10 to 28 carbon atoms and a moiety selected from the group consisting of
35 alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Ampholytic detergents include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight
40 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.

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Zwitterionic detergents include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds in which the aliphatic moieties can 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. Further use of zwitterionic detergents are discussed in US Patents Nos. 3,925,262 and 3,929, 678.

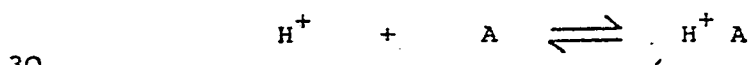
It is to be recognised that any of the foregoing detergents can be used separately herein or as mixtures.

A highly preferred mixture of surfactants is an anionic/nonionic mixture, especially a mixture of a C₈-C₂₂ alkyl benzene sulfonate and a C₁₀-C₂₀ alkanol ethoxylated with from 3 to 30 moles of ethylene oxide per mole of alkanol. Highly preferred mixtures include C₁₂ alkyl benzene sulfonate and C₁₄-C₁₅ alcohol-(7)-ethoxylate, in ratios of from 5:1 to 1:3, preferably 3:1 to 1:1. In still more preferred compositions, a fatty acid soap is added to the above-described mixture, preferably a C₁₀-C₂₀ soap at a level of from 1% to 5%.

Polycarboxylate Builder

A further essential component of the compositions of the invention is a polycarboxylate builder of a type in which the carboxylate anion of highest basicity has a logarithmic acidity constant (pK₁) of less than about 9, preferably of between about 2 and about 8.5, more preferably of between about 4 and about 7.5.

The logarithmic acidity constant is thus defined by reference to the equilibrium



where A is the fully ionized carboxylate anion of the builder salt.

The equilibrium constant is therefore

$$K_1 = \frac{[H^+ A]}{[H^+][A]}$$

and $pK_1 = \log_{10} K_1$

For the purposes of this specification, acidity constants are defined at 25°C and at zero ionic strength. Literature values are taken where possible (see Stability Constants of Metal-Ion Complexes, Special Publication No. 25, The Chemical Society, London); where doubt arises they are determined by potentiometric titration using a glass electrode. In the case

of polymeric polycarboxylate builders, the various carboxylate acidity constants are determined using the Katchalsky form of the Henderson-Hasselbach equation (see A Katchalsky and P. Spitnik, J. Polym. Sci., 1957, 23, 451).

- 5 Preferred carboxylates can also be defined in terms of their calcium ion stability constant ($pK_{Ca^{++}}$) defined, analogously to pK_1 , by the equations

$$pK_{Ca^{++}} = \log_{10} K_{Ca^{++}}$$

10

$$\text{where } K_{Ca^{++}} = \frac{[Ca^{++}][A]}{[Ca^{++}][A]}$$

15

Preferably, the polycarboxylate has a $pK_{Ca^{++}}$ in the range from about 2 to about 7 especially from about 3 to about 6. Once again literature values of stability constants are taken where possible. The stability constant is defined at 25°C and at zero ionic strength using a glass electrode method of measurement as described in Complexation in Analytical Chemistry by Anders Ringbom (1963).

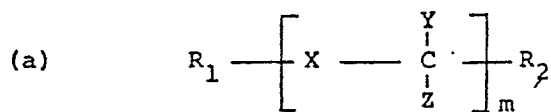
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The carboxylate or polycarboxylate builder can be monomeric, oligomeric or polymeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

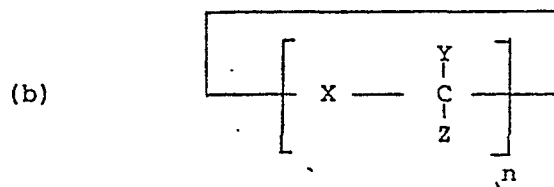
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Monomeric and oligomeric builders can be selected from acyclic, alicyclic heterocyclic and aromatic carboxylates having the general formulae

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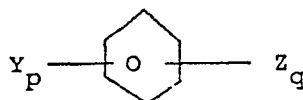


35



or

(c)



40

wherein R_1 represents $H; C_{1-30}$ alkyl or alkenyl optionally substituted by hydroxy, carboxy, sulfo or phosphono groups or attached to a polyethylenoxy moiety containing up to 20

ethyleneoxy groups; R_2 represents H ; C_{1-4} alkyl or alkenyl or hydroxy alkyl or alkaryl; sulfo; or phosphono groups; X represents a single bond; O ; S ; SO ; SO_2 ; or NR_1 ; Y represents H ; carboxy; hydroxy; carboxymethyloxy; or C_{1-30} alkyl or alkenyl optionally substituted by hydroxy or carboxy groups; Z represents H ; or carboxy; m is an integer from 1 to 10; n is an integer from 3 to 6; p, q are integers from 0 to 6, $p + q$ being from 1 to 6; and wherein X , Y , and Z each have the same or different representations when repeated in a given molecular formula.

Suitable carboxylates containing one carboxy group include lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgium Patents 821,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent 3,935,257 and the sulfinyl carboxylates described in Belgium Patent 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent 1,379,241, lactoxysuccinates described in British Patent 1,389,732, and aminosuccinates described in Netherlands Application 7,205,873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent 1,387,447.

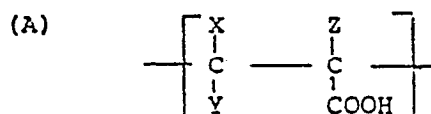
Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent 3,936,448, and the sulfonated pyrolysed citrates described in British Patent 1,082,179, while polycarboxylates containing phosphono substituents are disclosed in British Patent 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylate, cyclopentadienide

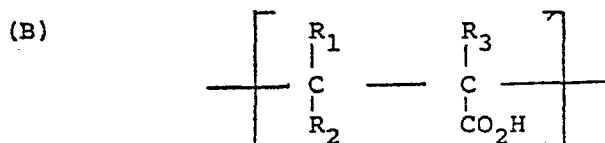
pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, manitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule.

Polymeric polycarboxylates suitable for use in the present compositions are preferably those homo- or copolymeric polycarboxylates having a molecular weight of at least 500 comprising carboxylic acid units, or salts thereof, having the general formulae:



wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, aryl, alkaryl, carboxyl, hydroxyl and carboxymethyl; at least one of X, Y, and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl and wherein only one of X, Y, and Z can be methyl, aryl, hydroxyl and alkaryl or



wherein R₁ and R₂ each represent a hydrogen atom or an alkyl group containing 1 to 3 carbon atoms, and R₃ represents H, OH or CH₃.

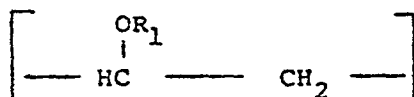
Polycarboxylates of type A include those derived from polyacid monomers selected from maleic acid, citraconic acid, aconitic acid, fumaric and, mesaconic acid, phenyl maleic acid, benzyl maleic acid, itaconic acid and methylene malonic acid, or the anhydrides thereof.

Polycarboxylates of type B include those derived, at

least in structural terms, from monoacid monomers selected from acrylic acid, α -hydroxyacrylic acid and methacrylic acid.

Preferably the above carboxyl monomer provides at least 45 mole percent of the monomeric species comprising the polymer species. The polymer can be selected from homopolymers of the above carboxyl monomers; or copolymers of two or more of the above carboxyl monomers; or copolymers of one or more of the above carboxyl monomers with an unsaturated polymerisable monomer other than the specified carboxyl monomers.

A preferred copolymer of the latter type comprises units having the general formula



wherein R_1 is a C_1 - C_{12} alkyl group or a C_1 - C_{12} acyl group, R_1 optionally being hydroxy or carboxy substituted (eg. $R_1 = \text{CH}_2\text{COOH}$)

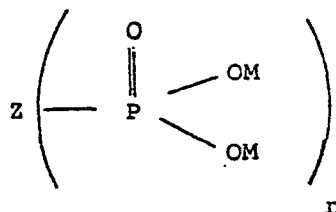
Examples of polycarboxylates in the above classes are sodium polymaleate (molecular weight 2,500), maleic acid/acrylic acid copolymer, 70:30 acrylic acid/hydroxy ethyl maleate copolymer, methylvinylether/maleic acid copolymer, ethylvinylether/maleic acid copolymer, sodium polymaleic acid sulfonate, 1:3 copolymer of acrylic acid and itaconic acid, a 1:4 copolymer of 3-butenic acid and methylenemalononic acid, a 1:9 copolymer of isocrotonic acid and citraconic acid, a 1:1.9 copolymer of methacrylic acid and aconitic acid, and a 1.2:1 copolymer of 4-pentenonic acid and itaconic acid.

The polymeric polycarboxylates have average molecular weight (generally measured as a viscosity average in 1 M NaOH as specified in Dutch Patent Application 78/04276) in the range from about 500 to about 2,000,000, and calcium stability constants in the range from about 2 to about 7.

The Polyphosphonate

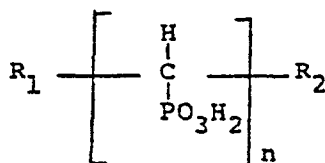
The preferred polyphosphonates have a calcium stability constant, $\text{pK}_{\text{Ca}^{++}}$, in the range from about 5 to about 10.5, desirably from about 6 to about 10 and especially from about 7.0 to about 9.5. The definition and method of measurement of stability constants has been more fully defined earlier.

Preferred polyphosphonates are those of the general formula

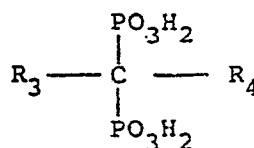


where n is at least 2, M is an alkali metal, ammonium or substituted ammonium cation and Z is a connecting organic moiety having an effective covalency equal to n . Preferably Z is a hydrocarbyl or a hydrocarbyl substituted amino radical. Various specific classes of polyphosphonates useful in the present invention, are indicated below.

The polyphosphonate can be derived from acids selected from the group consisting of those of the formulae:



(i)



(ii)

wherein R_1 and R_2 are hydrogen or CH_2OH ; n is an integer of from 3 to 10; R_3 is hydrogen, alkyl containing from 1 to about 20 carbon atoms, alkenyl containing from 2 to about 20 carbon atoms, aryl (e.g., phenyl and naphthyl), phenylethenyl, benzyl, halogen (e.g. chlorine, bromine, and fluorine), amino, substituted amino (e.g., dimethylamino, diethylamino, N-hydroxy-N-ethylamino, acetylamino), $-\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{PO}_3\text{H}_2$, $-\text{CH}(\text{PO}_3\text{H}_2)(\text{OH})$ or $-\text{CH}_2\text{CH}(\text{PO}_3\text{H}_2)_2$; and R_4 is hydrogen, lower alkyl (e.g., chlorine, bromine and fluorine), hydroxyl, $-\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{PO}_3\text{H}_2$, or $-\text{CH}_2\text{CH}_2\text{PO}_3\text{H}_2$.

Operable polyphosphonates of the above formula (i) include propane-1,2,3-triphosphonic acid; butane-1,2,3,4-tetraphosphonic acid; hexane-1,2,3,4,5,6-hexaphosphonic acid; hexane-1-hydroxy-2,3,4,5,6-pentaphosphonic acid; hexane-1,5-dihydroxy-2,3,4,5-tetraphosphonic acid; pentane-1,2,3,4,5-pentaphosphonic acid; heptane-1,2,3,4,5,6,7-heptaphosphonic acid; octane-1,2,3,4,5,6,7,8-octaphosphonic acid; nonane-1,2,3,4,5,6,7,8,9-nonaphosphonic acid; decane-1,2,3,4,5,6,-

7,8,9,10-decaphosphonic acid; and the salts of these acids, e.g., sodium, potassium, calcium, magnesium, ammonium, triethanolammonium, diethanolammonium, and monoethanolammonium salts.

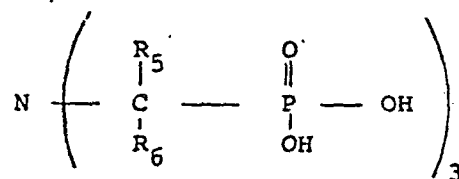
5 Among the operable polyphosphonates encompassed by the above formula (ii) are ethane-1-hydroxy-1, 1-diphosphonic acid; methanediphosphonic acid; methanehydroxydiphosphonic acid; ethane-1,1,2-triphosphonic acid; propane-1,1,3,3-tetraphosphonic acid; ethane-2-phenyl-1,1 diphosphonic
10 acid; ethane-2-naphthyl-1, 1-diphosphonic acid; methanepheryl-diphosphonic acid; ethane-1-amino-1, 1-diphosphonic acid; methanedichlorodiphosphonic acid; nonane-5,5-diphosphonic acid; n-pentane-1,1-diphosphonic acid; methanedifluorodiphosphonic acid; methanedibromodiphosphonic acid; propane-2,2-
15 diphosphonic acid; ethane-2-carboxy-1, 1-diphosphonic acid; propane-1-hydroxy-1,1,3-triphosphonic acid; ethane-2,hydroxy-1,1,2-triphosphonic acid; ethane-1-hydroxy-1,1,2-triphosphonic acid; propane-1,3-diphenyl-2, 2-diphosphonic acid, nonane-1, 1-diphosphonic acid; hexadecane-1, 1-diphosphonic acid; pent-
20 4-ene-1-hydroxy-1, 1-diphosphonic acid; octadec-9-ene-1-hydroxy-1,1-diphosphonic acid; 3-phenyl-1, 1-diphosphonoprop-2-ene; octane-1,1-diphosphonic acid; dodecane-1,1-diphosphonic acid; phenylaminomethanediphosphonic acid; naphthylamino-methane-diphosphonic acid; N,N-dimethylaminomethanediphosphonic
25 acid; N-(2-hydroxyethyl)-aminomethanediphosphonic acid; N-acetylaminomethanediphosphonic acid; aminomethanediphosphonic acid; and the salts of these acids, e.g., sodium, potassium, calcium, magnesium, ammonium, triethanolammonium, diethanolammonium and monoethanolammonium salts.

30 Mixtures of any of the foregoing phosphonic acids and/or salts can be used in the compositions of this invention. Methods of preparing these classes of materials are described in U.S. Patent No. 3,488,419.

35 For the purpose of this invention, it is preferred that the polyphosphonates are free of hydroxyl groups.

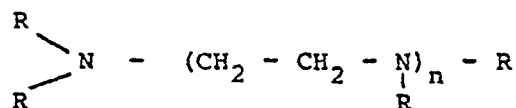
 Another useful and preferred class of polyphosphonates are the aminotrialkylidene phosphonates; these include acids of the general formula

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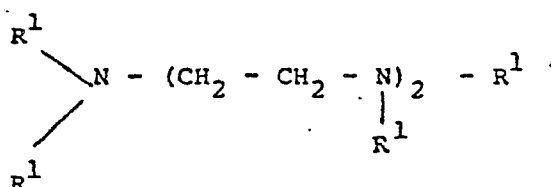
5 wherein R_5 and R_6 represent hydrogen or C_1 - C_4 alkyl radicals. Examples of compounds within this general class are aminotri-(methylenephosphonic acid), aminotri-(ethylidenephosphonic acid) and aminomono-(methylenephosphonic acid) di-(isopropylidenephosphonic acid).

10 Highly preferred polyphosphonates herein have the general formula



15 wherein n is an from 1 to 14, and each R is individually hydrogen or $CH_2PO_3H_2$ or a water-soluble salt thereof, provided that at least half of the radicals represented by R are $CH_2PO_3H_2$ radicals or water-soluble salts thereof. Especially preferred is the polyphosphonate having the

20 generally formula



25 wherein each R^1 is $CH_2PO_3H_2$ or a water-soluble salt thereof.

Other suitable polyphosphonates are those derived from triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and polyethyleneimines such as Montrex 600, a trade

30 mark of Dow Chemical Co., for a polyethyleneimine of molecular weight about 600.

The polyphosphonate is preferably added to the compositions of the invention at a level of at least 0.1% and generally at

40 a level in the range from about 0.2 to about 3.5 wt. %, more preferably from about 0.5 to about 2.2 wt. % of the composition.

Optional Components

It is to be understood that the compositions of the

45 invention may be supplemented by all manner of detergent components, either by including such components in the

aqueous slurry for spray drying or by admixing such components with the compositions of the invention following the drying step. Soil suspending agents at about 0.1% to 10% by weight such as water-soluble salts of carboxymethylcellulose, carboxy-
5 hydroxymethylcellulose, and polyethylene glycols having a molecular weight of about 400 to 10,000 are common components of the present invention. Compositions containing monomeric polycarboxylates as the builder component can also be supplemented by from about 0.1% to about 4% of the above defined
10 polymeric polycarboxylates as soil suspending agents, e.g. Gantrez AN119. Dyes, pigment optical brighteners, and perfumes can be added in varying amounts as desired. Suitable bleaches herein include percarbonates, perborates, and activators therefore.

15 Other materials such as fluorescers, antiseptics, germicides, enzymes in minor amounts, anti-caking agents such as sodium sulfosuccinate, and sodium benzoate may also be added. Enzymes suitable for use herein include those discussed in U.S. Patents 3,519,570 and 3,553,139 to McCarty and McCarty
20 et al issued 7 July, 1970 and 5 January, 1971 respectively.

Additional inorganic alkaline detergency builder salts can also be added, although high levels of highly alkaline builder salts and of phosphorus containing builder salts should be avoided. In particular, the solution pH of the
25 composition should be less than about 10, more preferably in the range from about 6 to about 9.5. The 'solution pH' is defined as the pH of a 1% solution in distilled water of the detergent composition.

Inorganic builder salts include, for instance, alkali
30 metal carbonates, tetraborates, pentaborates, aluminates, bicarbonates, sesquicarbonates, and water insoluble zeolites or alumino silicates. One such alumino silicate which is useful in the compositions of the invention is an amorphous water-insoluble hydrated compound of the formula $\text{Na}_x(\text{xAlO}_2 \cdot \text{ySiO}_2)$, wherein x is an integer of from 1 to 1.2 and y is 1,
35 said amorphous material being further characterized by a Mg^{++} exchange capacity of from about 50 mg eq. CaCO_3/g to about 150 mg eq. CaCO_3/g . This ion exchange builder is more fully described in Ireland published patent application 1505/74, to B.H. Gedge et al filed 16 July, 1974,
40 herein incorporated by reference.

A second water-insoluble synthetic aluminosilicate ion exchange material useful herein has the formula $\text{Na}_z (\text{AlO}_2)_z \cdot (\text{SiO}_2)_y \cdot x\text{H}_2\text{O}$, wherein z and y are integers of at least 6; the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264; said aluminosilicate ion exchange material having a particle size diameter from about 0.1 micron to about 100 microns; a calcium ion exchange capacity of at least about 200 mg eq./g; and a calcium ion exchange rate of at least about 2 grains/gallon/minute/gram as described in Belgian Patent 814,874 herein incorporated by reference.

Inorganic phosphate builders can also be included in the present compositions, although they should only be added in minor amounts such that the total phosphorus content is less than 6% and preferably less than 3% by weight of the composition. The polyphosphates can be selected from both chain polyphosphates such as tripolyphosphates, tetrapolyphosphate and pentapolyphosphate, and metaphosphates such as tetrametaphosphate, pentametaphosphate and hexametaphosphate. Higher polyphosphates having the empirical formulae $\text{Na}_{16}\text{P}_{14}\text{O}_{43}$ and $\text{Na}_{12}\text{P}_{10}\text{O}_{31}$ can also be used. Mixtures of chain polyphosphates and metaphosphate can also be used.

Preferred polyphosphates are the chain polyphosphates having from 3 to 9 preferably from 4 to 6 phosphorus atoms/molecule. A particularly suitable material is Phosphate Glass 627 (believed to be a sodium pentaphosphate) marketed by Albright and Wilson which is added in levels up to 10%, especially up to 4% by weight of the composition giving benefits particularly in particulate clay removal performance.

Organic carboxylates or polycarboxylates having pK_1 greater than 9 can also be added, eg., nitrilotriacetates or olefin/maleic acid copolymers. Such additional builders are preferably only present in small amounts, however, eg., up to about 8% by weight of the composition.

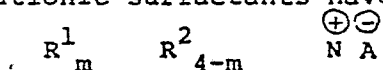
A further optional component of the present compositions is a suds depressant. Soap is an effective suds depressant, especially C_{16-22} soaps, for instance those derived by neutralisation of Hyfac (trade name) fatty acids. These are hardened marine fatty acids of chain length predominantly C_{18} to C_{20} . However, non-soap suds depressants are preferred. A preferred suds depressant comprises silicones. In particular, there may be employed a particulate suds depressant comprising silicone and silica releasably enclosed in a water soluble or water dispersible substantially non-surface active detergent-impermeable carrier. Suds depressing agents of this type are disclosed in

British Patent Specification 1,407,997 incorporated herein by reference.

A very suitable granular (prilled) suds depressant product comprises 7% silica/silicone (85% by weight silicated silica, 15% silicone obtained from Messrs. Dow Corning), 65% sodium tripolyphosphate, 25% tallow alcohol (EO)₂₅ (ie. condensed with 25 molar proportions of ethylene oxide), and 3% moisture. Also suitable and preferred is a combination of 0.02% to 5% by weight, especially about 0.3% of the composition, of a substantially water insoluble wax or mixture of waxes, melting at from 35°C to 125°C, and having saponification value less than 100, and a suds depressing amount, usually about 2% of the composition, of particulate suds depressant mentioned above.

Another desirable component of the compositions of the invention is a water-soluble cationic surfactant such as those described in European Patent Application No. 78 200 050.9.

incorporated herein by reference. The cationic surfactant, when used in combination with anionic and non-ionic surfactants in defined ratios and amounts, improves the oil stain detergency performance of the formulation. Preferred cationic surfactants have the general formula



wherein R^1 is selected from C₈₋₂₀ alkyl, alkenyl and alkaryl groups; R^2 is selected from C₁₋₄ alkyl, and benzyl; A is an anion; and m is 1, 2, or 3; provided that when m is 2, R^1 has less than 15 carbon atoms, and when m is 3, R^1 has less than 9 carbon atoms.

C₁₂ and C₁₄ alkyl trimethyl ammonium salts are highly preferred.

In preparing granular detergent compositions of the invention the components may be mixed together in any order and in powdery or in fluid form, eg. in an aqueous dispersion. The composition may be sprayed dried, drum dried, freeze dried or dried by other means, to provide a granular compo-

sition. Usually a moisture content of about 3% to about 10% is suitable to provide non-sticky free-flowing granules.

Liquid detergent compositions of the invention can contain, as optional ingredients, organic carriers or
5 solvents such as lower aliphatic alcohol having from 2 to 6 carbon atoms and 1 to 3 hydroxyl groups; ethers of diethylene glycol and lower aliphatic mono-alcohols having from 1 to 4 carbon atoms; and mixtures thereof. Liquid
10 compositions can also contain hydrotropes such as the water-soluble alkylaryl sulfonates having up to 3 carbon atoms in an alkyl group such as sodium, potassium, ammonium and ethanol amine salts of xylene-, toluene-, ethylbenzene- and isopropylbenzene sulfonic acids.

EXAMPLES 1-7

Built low-sudsing detergent compositions were prepared having the formulae given below. To make the products a slurry was prepared containing all the components except the bleach and enzyme and the slurry was then spray dried to form a granular intermediate. Bleach and enzyme were dry mixed with the intermediate granules to form the stated composition. All figures are given as % by weight.

EXAMPLE NO.	1	2	3	4	5	6	7
10 Sodium linear dodecyl benzene sulphonate	8.0	7.0	1.0	8.1	-	-	8.0
Dobanol 45-7 (9)	-	3.0	7.6	-	-	4.0	-
Sodium tallow alcohol sulphate	-	2.5	-	1.9	10.0	1.0	-
Sodium coconut soap	3.0	-	-	11.5	3.0	-	-
15 Sodium silicate (SiO ₂ : Na ₂ O 3.2:1)	6.1	4.2	-	-	-	6.0	4.2
Dobanol 45-4 (10)	-	-	4.0	-	2.0	8.0	-
Sodium alkyl (C ₁₄ -C ₁₆) triethoxysulphate	-	5.5	-	-	-	2.0	-
20 Sodium bicarbonate	-	12.0	-	-	15.0	-	10.0
Trisodium citrate	20.0	14.0	10.0	15.0	16.0	24.0	17.0
Sodium tripolyphosphate	-	5.0	15.0	2.0	-	-	8.0
Sodium perborate, tetra hydrate	10.0	-	5.0	15.0	-	-	-
25 Sodium carboxymethyl cellulose	0.8	0.8	0.8	0.8	0.8	0.8	1.4
Tallow Alcohol (EO) ₁₁	0.5	0.5	0.5	2.0	-	0.5	2.0
Silicone prills (1)	2.0	2.0	-	2.0	2.0	2.0	2.0
Microcrystalline wax (2)	0.3	0.3	0.5	0.3	0.3	0.3	0.3
Dequest 2060 (3)	-	-	1.5	1.0	-	-	-
Dequest 2040 (5)	1.0	-	-	0.5	-	1.0	2.0
Dequest 2010 (4)	-	1.0	-	-	1.0	-	-
Proteolytic enzyme (6)	-	1.0	-	-	0.5	-	0.8
Gantrez AN119 (7)	1.0	-	5.0	-	7.0	-	-
Gantrez AN139 (8)	-	2.0	0.5	-	-	1.0	-
Sodium Sulphate, water and miscellaneous	_____ to 100 _____						

NOTES:

(1) Comprising 0.14 parts by weight of an 85:15 by weight mixture of silanated silica and silicone, granulated with 1.3 parts of sodium tripolyphosphate, and 0.56 parts of tallow alcohol condensed with 25 molar proportions of ethylene oxide.

- (2) Witcodur 272 M.pt. 83°C. (Trade name)
- (3) Trade name for diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto.
- 5 (4) Trade name for ethane-1-hydroxy-1,1-diphosphonic acid, marketed by Monsanto
- (5) Trade name for ethylenediamine tetra (methylene phosphonic acid), marketed by Monsanto
- (6) Maxatase: 15% pure enzyme marketed by Gist Brocades.
- 10 (7) Trade name for maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of about 240,000 marketed by GAF. This was prehydrolysed with NaOH before addition.
- (8) Trade name for maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of about 500,000, marketed by GAF. This was prehydrolysed with NaOH before addition.
- 15 (9) Trade name: primary C₁₄₋₁₅ alcohols condensed with 7 molar proportions of ethylene oxide, marketed by Shell.
- 20 (10) Trade name: primary C₁₄₋₁₅ alcohols condensed with 4 molar proportions of ethylene oxide, marketed by Shell.
- These products provide excellent cleaning and whiteness maintenance performance particularly at low wash temperatures and on bleachable type stains.
- 25 Products with enhanced performance are obtained when the sodium alkyl benzene sulphonate is replaced by C₁₀₋₂₂ olefine sulphonates, C₁₀₋₂₀ paraffin sulphonates, and by zwitterionic detergents such as C₁₀₋₁₈ alkyl dimethyl ammonium propane sulphonate or hydroxypropane sulphonate.
- 30 Enhanced performance is also obtained when Gantrez AN119 is replaced by, as their sodium salts, a copolymer of methyl methacrylate and maleic acid, the molar ratio of the monomers being about 1:1, of molecular weight about 10,000; a 1:3 copolymer of acrylic acid and itaconic acid; a 1:4 copolymer of 3-butenic acid and methylenemalononic acid; a 1:9
- 35 copolymer of isocrotonic acid and citraconic acid; a 1.2:1 copolymer of 4-pentenoic acid and itaconic acid; and poly (α -hydroxy acrylic acid) having a molecular weight of about 50,000.
- 40 Enhanced performance is also obtained when, in the above examples, trisodium citrate is replaced by the same levels of

the water-soluble salts of lactic acid, glycollic acid, succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid, fumaric acid, aconitic acid, citraconic acid, carboxymethyloxy-succinic acid, lactoxysuccinic acid, 2-oxa-1,1,3-propane tri-carboxylic acid,

1,1,2,2-ethane-tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid, 1,1,2,3-propane tetracarboxylic acid, Citrex S5, marketed by Citrique Belge, cyclopentane-cis,cis, cis-tetracarboxylic acid, cyclopentadienide pentacarboxylic acid, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran - cis - dicarboxylic acid, 2,2,5, 5-tetrahydrofuran - tetracarboxylic acid, 1,2,3,4,5,6-hexane - hexacarboxylic acid, mellitic acid, or pyromellitic acid.

EXAMPLES 8-13

Granular detergent compositions were prepared having the following formulations.

	8	9	10	11	12	13
Linear C ₁₂ alkyl benzene sulphate	7.0	-	8.0	5.0	3.0	10.0
Myristyl trimethyl ammonium chloride	-	-	-	5.0	-	-
Tallow alcohol sulphate	3.0	-	-	-	-	-
Dobanol 45-E-7	-	8.0	2.4	1.5	3.0	-
Tallow alcohol (EO) ₁₁	3.0	-	-	-	-	1.0
Dobanol 45-E-4	-	4.0	-	-	-	-
C ₁₂ soap	-	2.0	-	-	2.0	-
C ₂₂ soap	2.0	-	3.0	4.0	-	2.0
Sodium tripolyphosphate	1.0	2.5	4.5	-	8.0	1.5
Sodium pentametaphosphate	-	-	-	1.5	-	-
Zeolite A (particle size 5 μ)	25.0	30.0	45.0	-	15.0	28.0
Gantrez AN 119	0.8	8.0	-	2.0	1.5	-
Gantrez AN 136	-	-	1.5	-	-	-
Dequest 2040	1.0	-	0.5	-	0.1	-
Dequest 2060	-	2.0	0.5	0.2	-	1.5
Sodium Silicate (SiO ₂ :Na ₂ O = 1.6)	3.0	4.0	5.0	-	4.0	7.0
Sodium citrate	15.0	10.0	20.0	16.0	6.0	10.0
Protease enzyme	0.5	0.5	-	0.5	-	0.5
Sodium perborate	-	-	-	5.0	-	10.0

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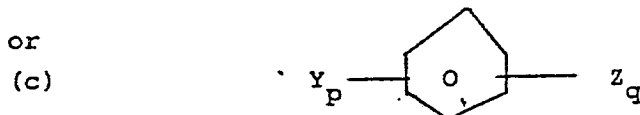
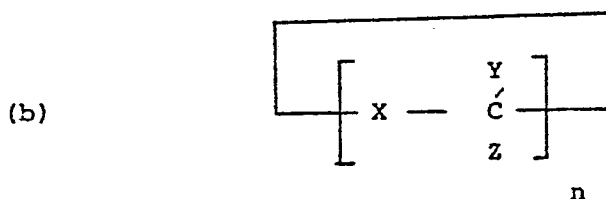
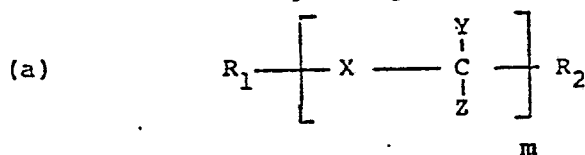
Sodium percarbonate	8.0	-	12.0	-	-	10.0
Sodium sulphate, moisture and miscellaneous	_____ to 100 _____					

5 The compositions of the above Examples all provide good
detergency performance, particularly on bleachable type soils and
stains and at low wash temperatures compared with compositions
containing no polyphosphonate material.

10 Similar results are achieved when the tripolyphosphate
is replaced by a P_{12} glassy phosphate. The anionic nonionic
active systems of Examples 10-13 can be replaced by all nonionic
systems, for example, with Dobanol 45-E-7 alone or with 8:1 mixtures
of, for example, Dobanol 45-E-7 and Dobanol 45-E-4. The Zeolite A
in Examples 8-10, 12 and 13 can be replaced in whole or in part by
an amorphous sodium aluminosilicate. Enhanced performance is also
15 obtained when lauryl trimethyl ammonium chloride is replaced by
myristyl trimethyl ammonium bromide, decyl trimethyl ammonium
chloride, dioctyl dimethyl ammonium bromide, lauryl dichloro-
benzyl dimethyl ammonium chloride, and cetyl trimethyl ammonium
ethosulphate. Enhanced performance is also obtained when trisodium
20 citrate is replaced by disodium succinate, trisodium carboxymethyl-
oxysuccinate, trisodium 2-oxa-1,1,3-propane-tricarboxylate, and
Citrex S-5.

CLAIMS

1. A detergent composition having a phosphorus content of no more than 6%, and a pH in 1% aqueous solution of less than 10 which comprises
 - (a) from 2 to 75% of an organic detergent selected from anionic, nonionic, amphoteric and zwitterionic detergents and mixtures thereof,
 - (b) from 4 to 50% of a carboxylate or polycarboxylate builder having a first carboxyl logarithmic acidity constant (pK_1) of less than 9, and
 - (c) from 0.01 to 4% of a polyphosphonic acid or salt thereof.
2. A composition according to Claim 1 in which the carboxylate builder has a pK_1 in the range from 2 to 8.5.
3. A composition according to Claim 1 or 2 having a pH in 1% aqueous solution in the range from 6 to 9.0.
4. A composition according to any preceding Claim in which the carboxylate builder has a logarithmic calcium stability constant in the range from 2 to 7.
5. A composition according to any preceding Claim in which the carboxylate builder is an organic monomeric or oligomeric, acyclic, alicyclic heterocyclic or aromatic carboxylate having the general formula



wherein R_1 represents $H;C_{1-30}$ alkyl or alkenyl optionally substituted by hydroxy, carboxy, sulfo or phosphono groups or attached to a polyethyleneoxy moiety containing up to 20 ethyleneoxy groups,

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R₂ represents H; C₁₋₄ alkyl or alkenyl or hydroxy alkyl or alkaryl; sulfo; or phosphono groups

X represents a single bond; O; S; SO; SO₂; or NR₁

Y represents H; carboxy; hydroxy; carboxymethyloxy; or C₁₋₃₀ alkyl or alkenyl optionally substituted by hydroxy or carboxy groups

Z represents H; or carboxy

m is an integer from 1 to 10

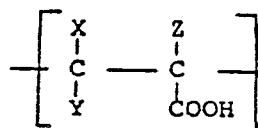
n is an integer from 3 to 6

p, q are integers from 0 to 6, p + q being from 1 to 6 and

wherein X, Y, Z each have the same or different representations when repeated in a given molecular formula.

6. A composition according to any preceding Claim in which the carboxylate builder is a water-soluble salt of citric acid, succinic acid, malonic acid, maleic acid, fumaric acid, glycollic acid, tartaric acid or lactic acid, or of a derivative of any said acid, or a mixture of said acid salts.

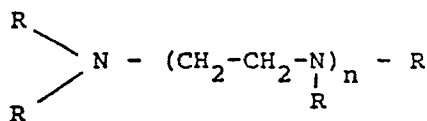
7. A composition according to any preceding Claim in which the carboxylate builder is a homo- or copolymeric polycarboxylate having a molecular weight of at least 500 comprising carboxylic acid units, or salts thereof, having the general formula:



wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, aryl, alkaryl, carboxyl, hydroxyl and carboxymethyl; at least one of X, Y, and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl and wherein only one of X, Y, and Z can be methyl, aryl, hydroxyl and alkaryl.

8. A composition according to any preceding Claim comprising from 3 to 30% of the carboxylate builder.

9. A composition according to any preceding Claim in which the polyphosphonate has the general formula



wherein N is an integer from 1 to 14 and each R is individually hydrogen or CH₂PO₃H₂ or a water-soluble salt thereof, provided that at least half of the radicals represented by R are

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$\text{CH}_3\text{PO}_3\text{H}_2$ or water-soluble salts thereof.

10. A composition according to any preceding Claim comprising from 0.2 to 3.5% of the polyphosphonic acid or salt thereof.



European Patent
Office

EUROPEAN SEARCH REPORT

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Application number

EP 78 200 190.3

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>DE - A - 2 310 620</u> (HENKEL) * claims 1 and 2 *	1,3,6 8, 10	C 11 D 3/ 00 C 11 D 3/ 36// C 11 D 3/395
-	<u>DE - A - 2 220 503</u> (SHELL) * claim 1 *	1	
A	<u>GB - A - 1 290 724</u> (HOECHST) --		
D	<u>GB - A - 1 439 000</u> (HENKEL)		
			TECHNICAL FIELDS SEARCHED (Int.Cl. ²)
			C 11 D 1/86 C 11 D 1/94 C 11 D 3/00 C 11 D 3/36 C 11 D 3/395
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
☒ The present search report has been drawn up for all claims			
Place of search Berlin		Date of completion of the search 29-11-1978	Examiner SCHULTZE