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(54) Detergent compositions.

(57) Granular detergent compositions comprising organic surfactant, phosphate detergency builder wherein at least 6% of the builder consists of a mixture of water-soluble orthophosphate and pyrophosphate salts, organic peroxyacid bleach precursor and specified polymeric polycarboxylic acids or salts thereof. The compositions provide improved low temperature cleaning together with excellent soil deposition and whiteness maintenance performance.

Croydon Printing Company Ltd.

DETERGENT COMPOSITIONS

John Hampton

This invention relates to built detergent compositions containing activators for oxygen releasing bleaching compounds, especially activators in the form of organic peroxy acid bleach precursors.

It is well known that peroxygen bleaching agents, e.g., perborates, percarbonates, perphosphates, persilicates etc., are highly useful for chemical bleaching of stains found on both colored and white fabrics. Such bleaching agents are most effective at high wash solution temperatures, i.e., above about 70°C. In recent years, attempts have been made to provide bleaching compositions that are effective at lower wash solution temperatures, i.e., between room temperature and 70°C. In consequence, bleaching agents have been investigated which exhibit their optimum bleach activity in this temperature range. These low temperature bleaches are useful in a variety of products intended for use under machine or hand-wash conditions, e.g., additive, pre-additive or soak-type laundry compositions as well as all-purpose detergent compositions.

A very effective class of low temperature bleach system comprises a peroxy bleach compound and an organic peracid precursor which react together to form the organic peracid in the wash solution. Examples of detergent compositions incorporating bleaching agents of this type are disclosed in U.S.P. 2,362,401 (Reicher et al), U.S.P. 3,639,248 (Moyer) and in British Patent Nos. 836,988 and 855,735.

It is also well known that compositions containing a significant amount of water-soluble orthophosphate and/or water-soluble pyrophosphate salts as builder can experience problems of soil deposition onto fabrics with resulting loss in fabric whiteness. Orthophosphates and pyrophosphates can occur as degradation products of sodium tripolyphosphate when the latter is incorporated in a detergent composition prepared by spray-drying. The extent of degradation during spray-drying, and therefore the level of orthophosphates and pyrophosphates, can very widely from as little as 3% up to about 40% or more by weight of tripolyphosphate, the actual degree of degradation being determined by the particular process conditions applied, notably crutcher mix moisture, temperature and residence time, the inlet temperature of the drying tower and the moisture of the blown powder.

Ortho and pyrophosphates are, of course, useful builders in their own right, and have come into more prominence in recentyears as the use of high levels of sodium tripolyphosphate has come under scrutiny because of the suspicion that soluble phosphate species accelerate the eutrophication or aging process of water bodies. This eutrophication is ordinarily evidenced by the rapid growth of algae in the water body. As more fully explained in German Offenlegungsschrift No. 2,605,052 ortho- and pyrophosphates, specially orthophosphate, can remove more hardness ions (Ca^{++}, Mg^{++}) per unit of P_2O_5 in their constitution than can tripolyphosphate. Orthophosphates, and to greater or less extent, pyrophosphates, act as detergency builders however, by precipitating these hardness ions as insoluble phosphates whereas sodium tripolyphosphate retains them in solution as complex ions. Building detergency by means of this precipitating mechanism tends, therefore, to cause undesirable effects, in particular, deposition of insoluble phosphate onto fabrics.

While the beneficial effects of both bleach activators and ortho/pyrophosphate builders are thus well known and a number of problems posed by the use of their materials have been explored, it has hitherto apparently not been recognized that bleach activators can have a deleterious effect on the soil deposition and whiteness maintenance characteristics of detergent composition containing significant levels of ortho/pyrophosphate builders. In as much as bleach activators would be expected to exert a solubilizing or dispersing effect on suspended soil, this observed soil deposition problem is considered most surprising.

Accordingly, it is an object of the present invention to provide a built detergent composition having improved low temperature bleaching performance together with undiminished soil deposition and whiteness maintenance characteristics.

According to the present invention there is provided a granular detergent composition characterized by:

(a) from about 2% to about 35% of organic surfactant selected from anionic, nonionic, amphoteric and zwitterinoic surfactants and mixtures thereof,

(b) from about 5% to about 90% of phosphate detergency builder comprising at least about 6% thereof of a mixture of water-soluble orthophosphate and pyrophosphate salts in a weight ratio of from 3:7 to 1:20,

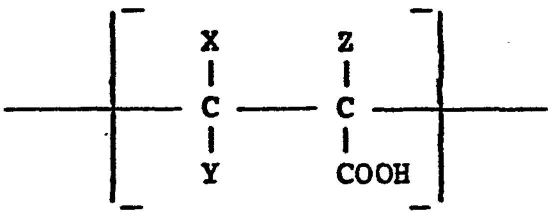
(c) from about 0.5% to about 20% of organic peroxy acid bleach precursor, and

(d) from about 0.1% to about 2% of a homo- or copolymeric polycarboxylic acid, or salt thereof, wherein the polycarboxylic acid comprises at least two carboxyl radicals separated from one another by not more than two carbon atoms.

In preferred compositions, the phosphate builder comprises from about 50% to about 90%, preferably from about 40% to about 88% of water-soluble tripolyphosphate salt and from about 10% to about 50%, preferably from about 12% to about 40% of the mixture of water-soluble orthophosphate and pyrophosphate salts in a weight ratio of from 3:7 to 1:20. While the builder can be present generally in the range from about 5% to about 90%, preferably about 10% to about 50%, highly preferred compositions are low in phosphate, containing phosphorus in am amount not exceeding that contained in about 28% anhydrous sodium tripolyphosphate. The benefits of the invention are readily apparent, however, even at builder:hardness ratios in excess of 1:1.

Preferred polymeric polycarboyxlic acids for use herein have an average molecular weight in the range from about 500 to about 2,000,000, more preferably from about 12,000 to about 1,500,000, and are copolymers comprising:

(a) polycarboxylic acid units having the general formula I

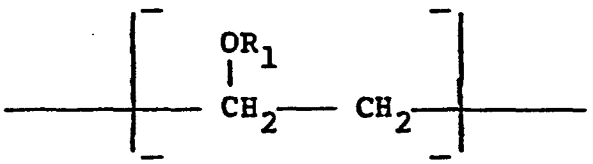


$$\left[-\overset{X}{\underset{Y}{C}}-\overset{Z}{\underset{COOH}{C}}- \right] \quad \text{I}$$

wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, aryl, alkaryl, carboxyl, hydroxy 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 carboxy-methyl only when Z is selected from carboxyl and carboxy-methyl and wherein only one of X, Y, and Z can be methyl, aryl, hydroxyl and alkaryl, and

(b) monomer units selected from

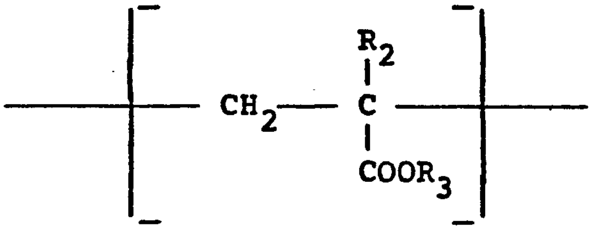
(a)



$$\left[-\overset{OR_1}{CH_2}-CH_2- \right] \quad \text{II}$$

wherein R_1 is a C_1 to C_{12} alkyl group or a C_1 to C_{12} acyl group, optionally being hydroxy substituted,

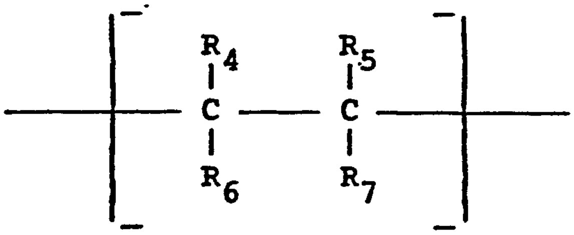
(b)



$$-\!\!\left[\; CH_2 - \underset{\substack{|\\ COOR_3}}{\overset{\substack{R_2\\ |}}{C}} \;\right]\!\!- \qquad \text{III}$$

wherein R_2 is H or CH_3 and R_3 is H, or a C_1 to C_{10} alkyl group, R_2, R_3 optionally being hydroxy substituted,

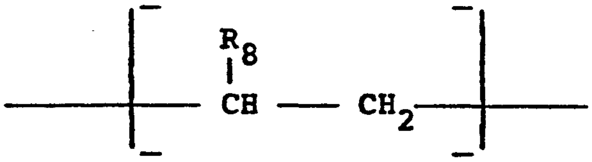
(c)



$$-\!\!\left[\; \underset{\substack{|\\ R_6}}{\overset{\substack{R_4\\ |}}{C}} - \underset{\substack{|\\ R_7}}{\overset{\substack{R_5\\ |}}{C}} \;\right]\!\!- \qquad \text{IV}$$

wherein each of R_4 to R_7 is H or an alkyl group such that R_4 to R_7 together have from 1 to 20 carbon atoms, R_4 to R_7 each optionally being hydroxy substituted, and

(d)



$$-\!\!\left[\; \overset{\substack{R_8\\ |}}{CH} - CH_2 \;\right]\!\!- \qquad \text{V}$$

in which R_8 is benzyl or pyrrolidone.

Highly preferred polymeric polycarboxylic acids are copolymers of maleic acid or maleic anhydride with methyl vinyl ether, ethyl vinyl ether, or acrylic acid having an average molecular weight in the range from about 12,000 to about 1,500,000. Moreover, the weight ratio of organic peroxy acid bleach precursor to polymeric carboyxlic acid preferably lies in the range from about 10:1 to about 1:3, more preferably from about 5:1 t about 1:2.

The compositions of the invention can take the form of an additive product for addition at the point of consumption either to a wash liquor or to an auxiliary composition containing a peroxy salt bleaching agent. More usually, however, the compositions of the invention will themselves contain peroxy salt bleaching agent in a level of from about 5% to about 35% by weight.

Other highly preferred ingredients of the present compositions include from 0.015% to 0.2% of a water-soluble magnesium salt additive (percentages expressed in terms of magnesium content), and from 0.05% to 0.4% (acid basis) of an aminopolyphosphonic acid, especially ethylenediamine-tetra(methylenephosphonic acid), diethylenetriaminepenta (methylenephosphonic acid) or salts thereof. These ingredients further serve to aid the low temperature cleaning performance of the present compositions and have a beneficial effect on fabric whiteness. The individual components of the compositions of the invention will now be discussed in detail.

An essential component of the present invention is an organic peroxy acid bleach precursor. Examples of the various classes are given below. Of these, highly preferred are bleach precursors providing peracetic acid bleach.

(a) Esters

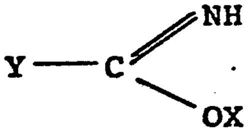
Esters suitable as peroxy compound precursors in the present invention include esters of monohydric substituted and unsubstituted phenols, substituted aliphatic alcohols in which the substituent group is electron withdrawing in character, mono- and disaccharides, N-substituted derivatives of hydroxylamine and esters of imidic acids. The phenol esters of both aromatic and aliphatic mono- and dicarboxylic acids can be employed. The aliphatic esters can have 1 to 20 carbon atoms in the acyl group, examples being phenyl laurate, phenyl myristate, phenyl palmitate and phenyl stearate. Of these, 1-acetoxy benzoic acid and methyl o-acetoxy benzoate are especially preferred. Diphenyl succinate, diphenyl azeleate and diphenyl adipate are examples of phenyl aliphatic dicarboxylic acid esters. Aromatic esters include phenyl benzoate, diphenyl phthalate and diphenyl isophthalate.

A specific example of an ester of a substituted aliphatic alcohol is trichloroethyl acetate. Examples of saccharide esters include glucose penta-acetate and sucrose octa-acetate. An exemplary ester of hydroxylamine is acetyl aceto hydroxamic acid.

These and other esters suitable for use as peroxy compound precursors in the present invention are fully described in British Patent Specification Nos. 836988 and 1147871.

A further group of esters are the acyl phenol sulphonates and acyl alkyl phenol sulphonates. An example of the former is sodium acetyl phenol sulphonate (alternatively described as sodium p-acetoxy benzene sulphonate). Examples of acyl alkyl phenol sulphonates include sodium 2-acetoxy 5-dodecyl benzene sulphonate, sodium 2-acetoxy 5-hexyl benzene sulphonate and sodium 2-acetoxy capryl benzene sulphonate. The preparation and use of these and analogous compounds is given in British Patent Specification Nos. 963135 and 1147871.

Esters of imidic acids have the general formula:-

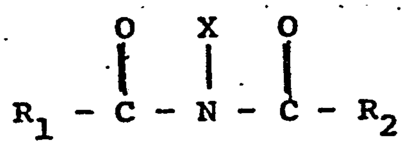


wherein X is substituted or unsubstituted C_1-C_{20} alkyl or aryl and Y can be the same as X and can also be $-NH_2$. An example of this class of compounds is ethyl benzimidate wherein Y is C_6H_5 and X is ethyl.

Other specific esters inlcude p-acetoxy acetophenone and 2,2-di-(4-hydroxyphenyl) propane diacetate. This last material is the diacetate derivative of 2,2-di(4-hydroxyphenyl) propane more commonly known as Bisphenol A which is an intermediate in the manufacture of polycarbonate resins. Bisphenol A diacetate and methods for its manufacture are disclosed in German DAS No. 1260479 published February 8th, 1968 in the name of VBB Chemiefaserwork Schwarza "Wilhelm Piesh".

(b) Imides

Imides suitable as organic peroxy compound precursors in the present invention are compounds of formula:-



$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle X}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-R_2$$

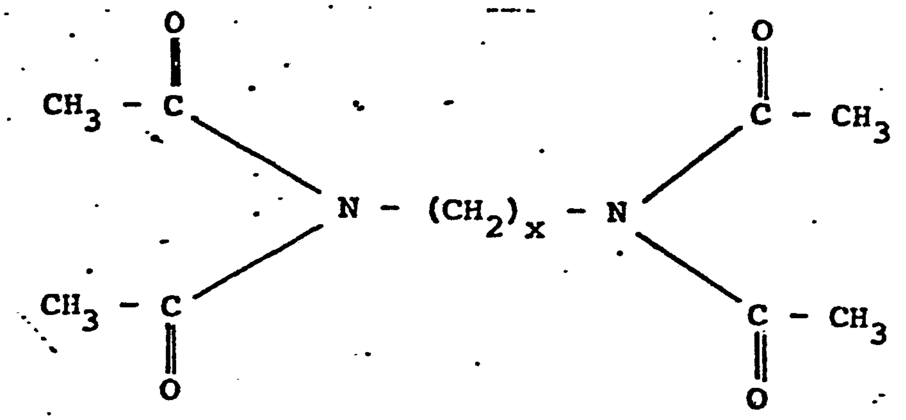
in which R_1 and R_2, which can be the same or different are independently chosen from a C_1-C_4 alkyl group or an aryl group and X is an alkyl, aryl or acyl radical (either carboxylic or sulphonic). Typical compounds are those in which R_1 is a methyl, ethyl, propyl or phenyl group but the preferred compounds are those in which R_2 is also methyl, examples of such compounds being N,N-diacetylaniline, N,N-diacetyl-p-chloroaniline and N,N-diacetyl-p-toluidine. Either one of R_1 and R_2 together with X may form a heterocyclic ring containing the nitrogen atom. An illustrative class having this type of structure is the N-acyl lactams, in which the nitrogen atom is attached to two acyl groups, one of which is also attached to the nitrogen in a second position through a hydrocarbyl linkage. A particularly preferred example of this class is N-acetyl caprolactam. The linkage of the acyl group to form a heterocyclic ring may itself include a heteroatom, for example oxygen, and N-acyl saccharides are a class of precursors of this type.

Examples of cyclic imides in which the reactive centre is a sulphonic radical are N-benzene sulphonyl phthalimide, N-methanesulphonyl succinimide and N-benzene sulphonyl succinimide. These and other N-sulphonyl imides useful herein are described in British Patent Specification No. 1242287.

Attachment of the nitrogen atoms to three acyl groups occurs in the N-acylated dicarboxylic acid imides such as the N-acyl phthalimides, N-acyl succinimides, N-acyl adipimides and N-acyl glutarimides. Imides of the above-mentioned types are described in British Patent Specification No. 855735 the disclosures of which are hereby incorporated specifically herein by reference.

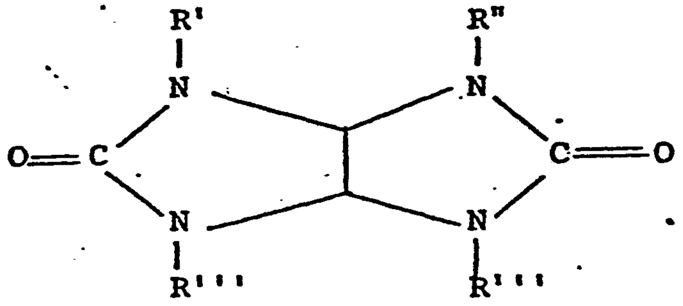
Two further preferred groups of materials in this class are those in which X in the above formula is either a second diacylated nitrogen atom i.e. substituted hydrazines, or a difunctional hydrocarbyl groups such as a C_1-C_6 alkylene group further substituted with a diacylated nitrogen atom i.e. tetra acylated alkylene diamines.

Particularly preferred compounds are N,N,N',N'-tetra acetylated compounds of formula:-



in which x can be 0 or an integer between 1 and 6, examples are tetra acetyl methylene diamine (TAMD) where $x=1$, tetra acetyl ethylene diamine (TAED) where $x=2$, and tetra acetyl hexamethylene diamine (TAHD) where $x=6$. Where $x=0$ the compound is tetra acetyl hydrazine (TAH). These and analogous compounds are described in British Patent Specification Nos. 907,356, 907,357, and 907,358.

Acylated glycourils form a further group of compounds falling within the general class of imide peroxy compound precursors. These materials have the general formula:-



in which at least two of the R groups represent acyl radicals having 2 to 8 carbon atoms in their structure. The preferred compound is tetra acetyl glycouril in which the R groups are all CH_3CO- radicals. The acylated glycourils are described in British Patent Specification Nos. 1246338, 1246339, and 1247429.

Other imide-type compounds suitable for use as peroxy compound precursors in the present invention are the N-(halobenzoyl) imides disclosed in British Patent Specification No. 1247857, of which N-m-chloro benzoyl succinimide is a preferred example, and poly imides containing an N-bonded-COOR group, e.g. N-methoxy carbonyl phthalimide, disclosed in British Patent Specification No. 1244200.

N-acyl and N,N'-diacyl derivatives of urea are also useful peroxy compound precursors for the purposes of the present invention, in particular N-acetyl dimethyl urea, N,N'-diacetyl ethylene urea and N,N'-diacetyl dimethyl urea. Compounds of this type are disclosed in Netherlands Patent Application No. 6504416 published 10th October, 1966. Other urea derivatives having inorganic persalt activating properties are the mono- or di-N-acylated azolinones disclosed in British Patent Specification No. 1379530.

Acylated hydantoin derivatives also fall within this general class of organic peroxy compound precursors. The hydantoins may be substituted e.g. with lower alkyl groups and one or both nitrogen atoms may be acylated. Examples of compounds of this type are N-acetyl hydantoin, N,N-diacetyl, 5,5-dimethyl hydantoin, 1-phenyl, 3-acetyl hydantoin and 1-cyclohexyl, 3-acetyl hydantoin. These and similar compounds are described in British Patent Specification Nos. 965672 and 1112191.

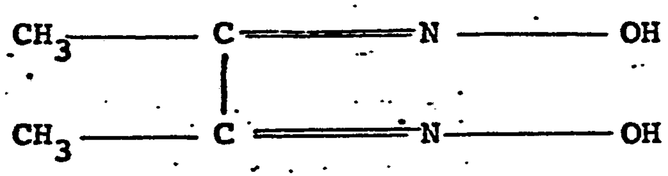
Another class of nitrogen compounds of the imide type are the N,N -diacyl methylene diformamides of which N,N-diacetyl methylamine diformamide is the preferred member. This material and analogous compounds are disclosed in British Patent Specification No. 1106666.

(c) Imidazoles

N-acyl imidazoles and similar five-membered ring systems form a further series of compounds useful as inorganic peroxy compound precursors. Specific examples are N-acetyl benzimidazole, N-benzoyl imidazole and its chloro- and methyl-analogues. Compounds of this type are disclosed in British Patent Specification Nos. 1234762, 1311765 and 1395760.

(d) Oximes

Oximes and particularly acylated oximes are also a useful class of organic peroxy compound precursors for the purpose of this invention. Oximes are derivatives of hydroxylamine from which they can be prepared by reaction with aldehydes and ketones to give aldoximes and ketoximes respectively. The acyl groups may be C_1-C_{12} aliphatic or aromatic in character, preferred acyl groups being acetyl, propionyl, lauroyl, myristyl and benzoyl. Compounds containing more than one carbonyl group can react with more than one equivalent of hydroxylamine and the commonest class of dioximes are those derived from 1,2-diketones and ketonic aldehydes, such as dimethyl glyoxime

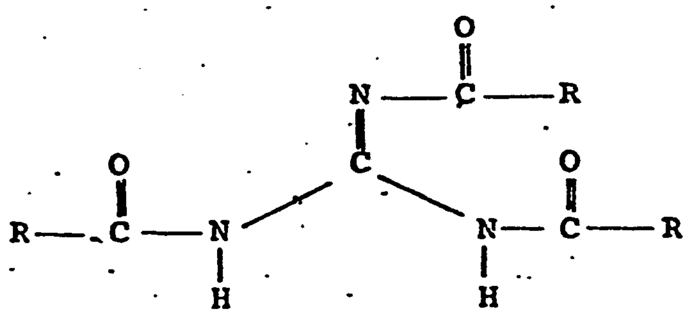


The acylated derivatives of this compound are of particular value as organic peroxy compound precursors, examples being diacetyl dimethyl glyoxime, dibenzoyl dimethyl glyoxime and phthaloyl dimethyl glyoxime.

(e) Carbonates

Substituted and unsubstituted aliphatic, aromatic and alicyclic esters of carbonic and pyrocarbonic acid have also been proposed as organic peroxy compound precursors. Typical examples of such esters are p-carboxy phenyl ethyl carbonate, sodium-p-sulphophenyl ethyl carbonate, sodium-p-sulphophenyl n-propyl carbonate and diethyl pyrocarbonate. The use of such esters as inorganic persalt activators in detergent compositions is set forth in British Patent Specification No. 970950.

In addition to the foregoing classes, numerous other materials can be utilised as organic peroxy compound precursors including triacyl guanidines of formula:-



wherein R is alkyl, preferably acetyl or phenyl, prepared by the acylation of guanidine salt. Other classes of compounds include acyl sulphonamides, e.g. N-phenyl N-acetyl benzene sulphonamide as disclosed in British Patent Specification No. 1003310 and triazine derivatives such as those disclosed in British Patent Specification Nos. 1104891 and 1410555. Particularly preferred examples of triazine derivatives are the di- and triacetyl derivatives of 2,4,6,-trihydroxy-1,3,5-triazine, 2-chloro-4,6-dimethoxy-S-triazine and 2,4-dichloro 6-methoxy-S-triazine. Piperazine derivatives such as 1,4-diacylated 2,5-diketo piperazine as described in British Patent Specification Nos. 1339256 and 1339257 are also useful as are water-soluble alkyl and aryl chloroformates such as methyl, ethyl and phenyl chloroformate disclosed in British Patent

Specification No. 1242106.

Of the foregoing classes of activators, the preferred classes are those that produce a peroxycarboxylic acid on reaction with an inorganic persalt. In particular the preferred classes are the imides, oximes and esters especially the phenol esters and imides.

Specific preferred materials are solid and are incorporated in the instant compositions in finely divided form, i.e., with an average particle size of less than about 500μ, more preferably less than about 250μ, especially less than about 150μ. Highly preferred materials include methyl o-acetoxy benzoate, sodium-p-acetoxy benzene sulphonate, Bisphenol A diacetate, tetra acetyl ethylene diamine, tetra acetyl hexamethylene diamine and tetra acetyl methylene diamine.

The essential phosphate builder component comprises at least 8% thereof of orthophosphate, and/or pyrophosphate salts, the remainder preferably consisting mainly of tripolyphosphate salts, in particular, the alkali metal, ammonium and substituted ammonium salts. The phosphate builder is present in the finished product at a level of from about 5% to about 90% by weight of the composition, preferably from about 8% to about 50%. The low phosphate compositions of the invention preferably contain phosphorus in an amount less than that contained in about 28% anhydrous sodium tripolyphosphate. The compositions of the invention will in general contain at least about 2%, especially at least about 3% by weight of the builder of orthophosphate salts, and/or at least about 6%, especially at least about 9% of the builder of pyrophosphate salts.

Suitable orthophosphate salts can be represented by the general formula

$$M_x H_{3-x} PO_4$$

wherein M is an alkali metal, ammonium or substituted ammonium cation, and x is 1, 2 or 3. Preferably M is sodium or potassium, especially sodium, although liquid detergent compositions of the invention can contain builder in the form of the ammonium or alkanolammonium salts, e.g., the salts formed from monoethanolamine, diethanolamine, triethanolamine and mixtures thereof. Normally, alkali metal salts are present in granular detergents in the form of crystalline hydrates having up to 12 moles of water associated with each mole of alkali metal phosphate. Ammonium and substituted ammonium salts can be obtained commercially or can be formed by neutralization of orthophosphoric acid or acid salt.

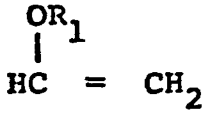
Pyrophosphate is an additional preferred component of the present invention. Readily available commercially are tetrasodium pyrophosphate $Na_4P_2O_7$ and its decahydrate $Na_4P_2O_7.10H_2O$, tetrapotassium pyrophosphate $K_4P_2O_7$, sodium acid pyrophosphate or "acid pyro" $Na_2H_2P_2O_7$ and its hexahydrate $Na_2H_2P_2O_7.6H_2O$, and pyrophosphoric acid $H_4P_2O_7$. Monosodium pyrophosphate and trisodium pyrophosphate also exist, the latter as the anhydrous form or the mono- or nona-hydrate. The generic formula for the anhydrous forms of these compounds can be expressed as $M_xH_yP_2O_7$, where M is alkali metal and x and y are integers having the sum of 4.

With regard to the polymeric polycarboxylates, these are suitably derived from polycarboxylates selected from maleic acid, citraconic acid, aconitic acid, fumaric acid, mesaconic acid, phenyl maleic acid, benzyl maleic acid, itaconic acid and methylene malonic acid monomers, or from the anhydrides of the above monomers where these exist.

Preferably the polycarboxyl monomer provides at least about 15, more preferably at least about 33, especially at least about 45 moles percent of the monomeric species comprising the polymer species. The polymer can be selected from homopolymers of the above polycarboxyl monomers; or copolymers of two or more of the above polycarboxyl monomers; or copolymers of one or more of the above polycarboxyl monomers with an unsaturated polymerisable monomer other than the specified polycarboxyl monomers.

In general terms, suitable polymerizable unsaturated monomers include

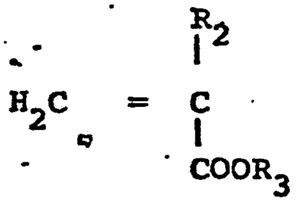
(a)



$$HC(OR_1)=CH_2$$

wherein R_1 is a C_1 to C_{12} alkyl group or a C_1 to C_{12} acyl group, R_1 optionally being hydroxy substituted,

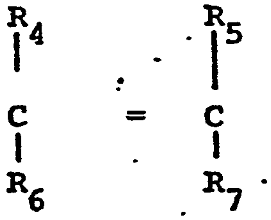
(b)



$$H_2C=C(R_2)(COOR_3)$$

wherein R_2 is H or CH_3 and R_3 is H, or a C_1 to C_{10} alkyl group, R_2, R_3 optionally being hydroxy substituted,

(c)



$$R_4R_6C=CR_5R_7$$

wherein each of R_4 to R_7 is H or an alkyl group such that R_4 to R_7 together have from 1 to 20 carbon atoms, R_4-R_7 each optionally being hydroxy substituted.

(d)

N-vinyl pyrrolidone styrene.

Highly preferred polymeric polycarboxylates in the present invention are the copolymers of maleic acid with the above unsaturated monomers, optionally wholly or partly neutralised by sodium or potassium. All may be made by heating together maleic anhydride and the other monomer in an appropriate solvent, such as benzene, cyclohexene, or in some cases in excess of one of the monomers, in the presence of a catalyst such as an organic peroxide or azo-bisbutyronitrile. As will be appreciated by those skilled in the art, different solvents, catalysts, and reaction conditions are most suitable according to the type of copolymer and molecular weight thereof being prepared. In particular in order to make the high molecular weight polymers for the present invention, it is often desirable to use up the initiator (catalyst) to make a macro-radical and then to add further monomers employing the macro-radical as sole initiator. Methods of preparing these compounds are described in U.S. Patent No. 2,430,313 (Vana to E.I. Dupont de Nemours Co.). The polymers so prepared are, of course, copolymers of maleic anhydride and the selected monomer. Either before or during the manufacture of the compositions of the invention, these are usually hydrolysed to the acid form and optionally neutralised as indicated above.

In the present specification, unless stated otherwise, the molecular weight of the polymeric polycarboxylate is expressed as that of the unneutralised acid form thereof. Generally, the average molecular weight falls in the range from about 500 to about 2,000,000.

The alkyl vinyl ethers of class (a) above are preferably methyl vinyl ethers. Preferred molecular weights for these copolymers are in the range from 12,000 to 1,500,000, more preferably 50,000 to 300,000. Copolymers in anhydride form believed to be of this class are commercially available from GAF Corporation under the trade names Gantrez AN119 (MWt. 200,000 in anhydride form), Gantrez AN139 (MWt. 500,000 in anhydride form), AN149 (MWt. 750,000 in anhydride form) and AN169 (MWt. 1,125,000 in anhydride form). Ethyl and methyl vinyl ether/maleic anhydride copolymers are also available from BASF under the trade name Sokalan and having molecular weight about 30,000.

The molecular weight of these copolymers is the viscosity average molecular weight and is determined as follows:

A number of polymer solutions of known concentration (<1% w/v) are made up in a suitable solvent and their viscosities determined as described in F. Daniels et al Experimental Physical Chemistry pp 71-74, 242-246, McGraw-Hill (1949), at 25°C, using an Ostwald viscometer. A plot of (specific viscosity/concentration) against concentration is then constructed and the best line extrapolated to zero concentration. The value of (specific viscosity/concentration) at zero concentration is termed the intrinsic viscosity, $[\eta]$. This parameter is used to determine a viscosity-average molecular weight, $\bar{M}_v$.

For the above copolymers as anhydrides the equation applicable employing acetone as solvent, and giving the molecular weight of the anhydride form is:

$$\log[\eta] = 0.94 \log \bar{M}_v - 3.27 \qquad \text{I}$$

In 1M NaOH, giving the molecular weight of the sodium salt of the copolymer, the equation is:

$$\log[\eta] = 0.86 \log \bar{M}_v - 2.88 \qquad \text{II}$$

The acrylic-maleic copolymer derived from monomers of class (b) above are preferably based upon acrylic acid or methyl methacrylate, although higher alkyl esters can be employed. The manufacture of these polymers, and the control of the molar ratio of the monomers one to other is described by Seymour, Harris and Branum in Industrial and Engineering Chemistry, Volume 41, pages 1509 to 1513, 1949. Preferably copolymers wherein the molar ratio of acrylate ester to maleic acid is from about 4:1 to 1:1 are employed herein; their molecular weight is preferably in the range from 3,000 to 1,500,000, especially from about 12,000 to 100,000.

The molecular weight of these copolymers is determined by the method described above.

When an olefin of class (c) is used, the copolymers are preferably of high molecular weight and are preferably based on ethylene. The preferred molecular weight range is from 275,000 to 1,500,000.

Another preferred group of materials within this class are copolymers of maleic anhydride or acid with propylene, isobutylene, alkyl substituted isobutylene and, especially, di-isobutylene, having molecular weight in the range from about 500 to 50,000 and molar ratio of olefine to maleic acid in the range from 1:1 to 1:2. Suitable materials of this type are available under the trade names "Empicryl" of Albright and Wilson Limited, and "Orotan" of Rohm and Haas.

The molecular weight of these polymers is determined by the method described above but employing ethanol as solvent and using the equation:

$$\log[\eta] = 1.18 \log \bar{M}_v - 3.85 \qquad \text{III}$$

The vinyl pyrrolidone maleic copolymers preferably have molecular weight in the range from about 3,000 to 50,000, especially about 20,000 to 30,000. The molecular weight is determined by the method described above but employing 1M NaOH as solvent and using the equation II above.

The styrene-maleic acid copolymers preferably have molecular weight about 300,000. The molecular weight is determined by the same method but employing acetone as solvent and using the equation I above.

The most preferred copolymers are those of methyl and ethyl vinyl ether-maleic anhydride or acid described above.

A further essential ingredient of the detergent compositions of the invention is a surfactant selected from anionic, nonionic, zwitterionic or ampholytic surfactants. The surfactant is present at a level of from about 2% to about 35%, more preferably from about 3% to about 20% of the composition. A typical listing of the classes and species of these surfactants is given in U.S. Patent 3,663,961 issued to Norris on May 23, 1972, and incorporated herein by reference.

Suitable synthetic anionic surfactants are water-soluble salts of alkyl benzene sulfonates, alkyl sulfates, alkyl polyethoxy ether sulfates, paraffin sulfonates, alpha-olefin sulfonates, alpha-sulfo-carboxylates and their esters, sulfonates, alpha-sulfo-carboxylates and their esters, alkyl glyceryl ether sulfonates, fatty acid monoglyceride sulfates and sulfonates, alkyl phenol polyethoxy ether sulfates, 2-acyloxy-alkane-1-sulfonate, and beta-alkyloxy alkane sulfonate.

A particularly suitable class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts or organic sulfuric reaction products having in their molecular structure an alkyl or alkaryl 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_{8-18}) 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, especially about 11 to about 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S.P. 2,220,099 and 2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). 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.

Other anionic detergent compounds herein include the sodium C_{10-18} 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 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 or esters of α-sulfonated fatty acids containing from about 6 to 20 carbon atoms in 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 about 10 to 18, especially about 12 to 16, carbon atoms in the alkyl group and from about 1 to 12, especially 1 to 6, more especially 1 to 4 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24, preferably about 14 to 16, carbon atoms, especially those made by reaction with sulfur trioxide followed by neutralization under conditions such that any sultones present are hydrolysed to the corresponding hydroxy alkane sulfonates; water-soluble salts of paraffin sulfonates containing from about 8 to 24, especially 14 to 18 carbon atoms, and β-alkyloxy 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.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred. Magnesium and calcium are preferred cations under circumstances described by Belgian patent 843,636 invented by Jones et al, issued December 30, 1976. Mixtures of anionic surfactants are contemplated by this invention; a preferred mixture contains alkyl benzene sulfonate having 11 to 13 carbon atoms in the alkyl group or paraffin sulfonate having 14 to 18 carbon atoms and either an alkyl sulfate having 8 to 18, preferably 12 to 18, carbon atoms in the alkyl group, or an alkyl polyethoxy alcohol sulfate having 10 to 16 carbon atoms in the alkyl group and an average degree of ethoxylation of 1 to 6.

Nonionic surfactants suitable for use in the detergent component of the present composition include compounds produced by the condensation of ethylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyethylene 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 surfactants include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. 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 3 to 30, preferably 5 to 14 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 9 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 11 moles of ethylene oxide per mole of phenol; nonylphenol and di-isooctylphenol condensed with 13 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 3 to about 30 moles, preferably 5 to about 14 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 3 and 30, desirably between 5 and 14 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or, prepared by the Ziegler process from ethylene, e.g. 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 (Synperonic 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 45-9, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 14, 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 with an average of between 7 and 12 moles of ethylene oxide 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 15 carbon atoms in the alkyl group and up 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 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.

The addition of a water-soluble cationic surfactant to the present compositions has been found to be useful for improving the greasy stain removal performance. Suitable cationic surfactants are those having a critical micelle concentration for the pure material of at least 200 ppm and preferably at least 500 ppm specified at 30°C and in distilled water. Literature values are taken where possible, especially surfact tension or conductimetric values - see Critical Micelle Concentrations of Aqueous Surfactant System, P. Mukerjee and K.J. Mysels, NSRDS - NBS 37 (1971).

A highly preferred group of cationic surfactants of this type have the general formula:-

$$R^1_m R^2_{4-m} N \quad Z$$

wherein R^1 is selected from C_{8-20} alkyl, alkenyl and alkaryl groups; R^2 is selected from C_{1-4} alkyl and benzyl groups; Z is an anion in number to give electrical neutrality; 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.

Where m is equal to 1, it is preferred that R^2 is a methyl group. Preferred compositions of this mono-long chain type include those in which R^1 is C_{10} to C_{16} alkyl group. Particularly preferred compositions of this class include C_{12} alkyl trimethylammonium halide and C_{14} alkyl trimethylammonium halide.

Where m is equal to 2, the R^1 chains should have less than 14 carbon atoms. Particularly preferred cationic materials of this calss include di-C_8 alkyldimethylammonium halide and di-C_{10} alkyldimethylammonium halide materials.

Where m is equal to 3, the R^1 chains should be less than 9 carbon atoms in length. An example is trioctyl methyl ammonium chloride.

Another highly preferred group of cationic compounds have the general formula: .

$R^1R^2_mR^3_{3-m}N^+A$ wherein R^1 represents a C_{6-24} alkyl or alkenyl group or a C_{6-12} alkaryl group, each R^2 independently represents a $(C_nH_{2n}O)_xH$ group where n is 2, 3 or 4 and x is from 1 to 14, the sum total of $C_nH_{2n}O$ groups in R^2_m being from 1 to 14, each R^3 independently represents a C_{1-12} alkyl or alkenyl group, an aryl group or a C_{1-6} alkaryl group, m is 1, 2 or 3, and A is an anion.

In this group of compounds, R^1 is selected from C_{6-24} alkyl or alkenyl groups and C_{6-12} alkaryl groups; R^3 is selected from C_{1-12} alkyl or alkenyl groups and C_{1-6} alkaryl groups. When m is 2, however, it is preferred that the sum total of carbon atoms in R^1 and R^3_{3-m} is no more than about 20 with R^1 representing a C_{8-18} alkyl or alkenyl group More preferably the sum total of carbon atoms in R^1 and R^1_{3-m} is no more than about 17 with R^1 representing a C_{10-16} alkyl or alkenyl group. When m is 1, it is again preferred that the sum total of carbon atoms in R^1 and R^3_{3-m} is no more than about 17 with R^1 representing a C_{10-16} alkyl or alkaryl group.

Additionally in this group of compounds, the total number of alkoxy radicals in polyalkoxy groups (R^2_m) directly attached to the cationic charge centre should be no more than 14. Preferably, the total number of such alkoxy groups is from 1 to 7 with each polyalkoxy group (R^2) independently containing from 1 to 7 alkoxy groups; more preferably, the total number of such alkoxy groups is from 1 to 5 with each polyalkoxy group (R^2) independently containing from 1 to 3 alkoxy groups. Especially preferred are cationic surfactants having the formula:

$$R^1 \quad (C_nH_{2n}OH)_m \quad (CH_3)_{3m} \overset{+}{N} A$$

wherein R^1 is as defined immediately above, n is 2 or 3 and m is 1, 2 or 3.

Particularly preferred cationic surfactants of the class having m equal to 1 are dodecyl dimethyl hydroxyethyl ammonium salts, dodecyl dimethyl hydroxypropyl ammonium salts, myristyl dimethyl hydroxyethyl ammonium salts and dodecyl dimethyl dioxyethylenyl ammonium salts. When m is equal to 2, particularly preferred cationic surfactants are dodecyl dihydroxyethyl methyl ammonium salts, dodecyl dihydroxypropyl methyl ammonium salts, dodecyl dihydroxyethyl ethyl ammonium salts, myristyl dihydroxyethyl methyl ammonium salts, cetyl dihydroxyethyl methyl ammonium salts, stearyl dihydroxyethyl methyl ammonium salts, oleyldihydroxyethyl methyl ammonium salts, and dodecyl hydroxy ethyl hydroxypropyl methyl ammonium salts. When m is 3, particularly preferred cationic surfactants are dodecyl trihydroxyethyl ammonium salts, myristyl trihydroxyethyl ammonium salts, cetyl trihydroxyethyl ammonium salts, stearyl trihydroxyethyl ammonium salts, oleyl trihydroxy ethyl ammonium salts, dodecyl dihydroxyethyl hydroxypropyl ammonium salts and dodecyl trihydroxypropyl ammonium salts.

In the above, the usual inorganic salt counterions can be employed, for example, chlorides, bromides and borates. Salt counterions can also be selected from organic acid anions, however, such as the anions derived from organic sulphonic acids and from sulphuric acid esters. A preferred example of an organic acid anion is a C_{6-12} alkaryl sulphonate.

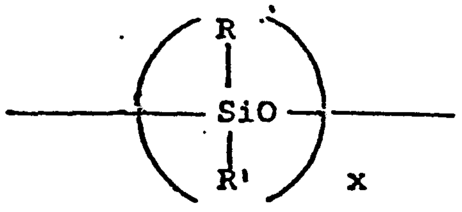
Of all the above cationic surfactants, especially preferred are dodecyl dimethyl hydroxyethyl ammonium salts and dodecyl dihydroxyethyl methyl ammonium salts.

Additional preferred cationic surfactants are fully disclosed in British Patent Application No. 79-25946 and incorporated herein by reference.

The above water-soluble cationic surfactants can be employed in nonionic/cationic surfactant mixtures in a weight ratio of from about 10:6 to about 20:1, more preferably from about 10:2 to about 10:6, and particularly from about 10:3 to 10:5.

Other optional ingredients which can be added to the present composition include suds modifiers, chelating agents, anti-redeposition and soil suspending agents, optical brighteners, bactericides, anti-tarnish agents, enzymatic materials, fabric softeners, antistatic agents, perfumes, antioxidants and bleach catalysts.

U.S. Patent 3,933,672 issued January 20, 1976, to Bartollota et al., incorporated herein by reference, discloses a silicone suds controlling agent. The silicone material can be represented by alkylated polysiloxane materials such as silica aerogels and xerogels and hydrophobic silicas of various types. The silicone material can be described as siloxane having the formula:



$$-\left(\begin{array}{c} R \\ | \\ SiO \\ | \\ R' \end{array}\right)_x-$$

wherein x is from about 20 to about 2,000 and R and R' are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl and phenyl. The polydimethylsiloxanes (R and R' are methyl) having a molecular weight within the range of from about 200 to about 2,000,000, and higher, are all useful as suds controlling agents. Additional suitable silicone materials wherein the side chain groups R and R' are alkyl, aryl, or mixed alkyl or aryl hydrocarbyl groups exhibit useful suds controlling properties. Examples of the like ingredients include diethyl-, dipropyl-, dibutyl-, methyl-, ethyl-, phenylmethylpolysiloxanes and the like. Additional useful silicone suds controlling agents can be represented by a mixture of an alkylated siloxane, as referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from about 10 millimicrons to 20 millimicrons and a specific surface area above about 50 m^2/g. intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2. The silicone suds suppressing agent is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier.

Particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2,646,126 published April 28, 1977 and incorporated herein by reference. An example of such a compound is DS-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

Suds modifiers as described above are used at levels of up to approximately 5%, preferably from 0.1 to 2% by weight of the nonionic surfactant. They can be incorporated into the particulates of the present invention or can be formed into separate particulates that can then be mixed with the particulates of the invention. The incorporation of the suds modifiers as separate particulates also permits the inclusion therein of other suds controlling materials such as C_{20}-C_{24} fatty acids, microcrystalline waxes and high MWt copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al U.S. Patent No. 3,933,672.

The detergent compositions of the invention can also contain supplemental detergency builders such as organic builders and aluminosilicates.

Examples of suitable organic alkaline detergency builder salts are:

(1) water-soluble amino polyacetates, e.g. sodium and potassium ethylendiaminetetraacetates, nitrilotriacetates, and N-(2-hydroxyethyl)nitrilodiacetates;

(2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates;

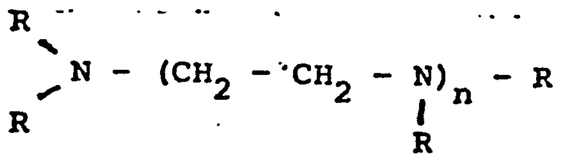
(3) water-soluble polyphosphonates, including, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium salts of methylenediphosphonic acid and the like.

(4) water-soluble polycarboxylates such as the salts of lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgian Patents 821,368, 821,369 and 821,370; succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid,

aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; 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, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent 1,425,343.

A further class of builder salts is the insoluble alumino silicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation $Na_z(AlO_2)_z(SiO_2)_y.xH_2O$ 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. Compositions incorporating builder salts of this type form the subject of British Patent Specification No. 1,429,143 published March 24, 1976, German Patent Application No. OLS 2,433,485 published February 6, 1975, and OLS 2,525,778 published January 2, 1976, the disclosures of which are incorporated herein by reference.

The detergent compositons of the invention can also be supplemented by bleaches, especially sodium perborate tetrahydrate or sodium percarbonate at levels from about 5% to about 35%. The compositions also preferably include from about 0.05% to about 0.6% (acid basis), preferably from about 0.06% to about 0.3% of aminopolyphosphonic acid, or salt thereof, having the general formula:



$$\begin{matrix}R \\ \\ R\end{matrix}\!\!>N-(CH_2-CH_2-\underset{R}{\underset{|}{N}})_n-R$$

wherein n is an integral number from 0 to 3, and each R is individually hydrogen or $CH_2PO_3H_2$ provided that at least half of the radicals represented by R are $CH_2PO_3H_2$. Preferred aminopolyphosphonic acids are selected from nitrilotri(methylenephosphonic acid), ethylene-diaminetetra(methylenephosphonic acid), diethylenetriamine(pentamethylenephosphonic acid), and mixtures thereof.

An alkali metal, or alkaline earth metal, silicate can also be present. The alkali metal silicate is preferably from about 3% to about 8%. Suitable silicate solids have a molar ratio of SiO_2/alkali $metal_2O$ in the range from about 1.0 to about 3.3, more preferably from 1.5 to 2.0. Other suitable ingredients include soil-suspending agents such as the water-soluble salts of carboxymethyl cellulose and of methyl vinylether/maleic anhydride copolymer, nonionic cellulose materials such as hydroxyethyl cellulose, and polyethylene glycols.

In the Examples which follow, the abbreviations used have the following designation:

LAS : Linear C_{12} alkyl benzene sulphonate
TAS : Sodium tallow alcohol sulfate
$TlAE_n$: Tallow alcohol ethoxylated with n moles of ethylene oxide per mole of alcohol
CTMAC : Coconut trimethyl ammonium chloride
Dobanol 45-E-7 : A C_{14-15} oxo-alcohol with 7 moles of ethylene oxide, marketed by Shell

Dobanol 45-E-4	: A C_{14-15} oxo-alcohol with 4 moles of ethylene oxide, marketed by Shell
TAED	: Tetraacetyl ethylene diamine
AOBS	: Sodium p-acetoxy benzene sulphonate
TAHD	: Tetraacetyl hexamethylene diamine
Silicate	: Sodium silicate having an $SiO_2:Na_2O$ ratio of 1.6.
Wax	: Microcrystalline wax - Witcodur 272 M.pt 87°C
Silicone Prill	: 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
5 Gantrez AN119	: 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.
Gantrez AN139	: Trade Name for maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of about 500,000, marketed by GAF.
Empicryl	: Trade Name, believed to be a copolymer of diisobutylene and maleic acid, MWt about 5000.
Brightener	: Disodium 4,4'-bis(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene-2:2'-disulphonate.
Dequest 2060	: Trade Name for diethylene triamine penta(methylene phosphonic acid), marketed by Monsanto.
Dequest 2041	: Trade Name for ethylenediamine tetra (methylene phosphonic acid), marketed by Monsanto.

The present invention is illustrated by the following examples:-

EXAMPLES I - XII

Built detergent compositions are prepared having the formulae given below.

	EXAMPLES					
	I	II	III	IV	V	VI
LAS	8.0	8.0	5.0	8.0	4.0	7.0
TAS	4.0	2.0	-	-	2.0	-
CTMAC	-	-	2.0	-	-	-
Silicate	2.0	6.0	8.0	-	6.0	-
Dobanol 45-E-7	-	-	3.0	3.0	8.0	4.0
Dobanol 45-E-4	-	-	-	-	-	4.0
Disodium orthophosphate	1.0	0.5	1.0	0.8	1.0	1.0
Sodium coconut soap	-	-	-	-	12.0	-
Tetrasodium pyrophosphate	5.0	2.0	7.0	2.4	7.0	4.0
Magnesium silicate (SiO_2:MgO ratio 1:1)	2.0	-	-	-	-	-
Pentasodium tripolyphosphate	15.0	21.0	25.0	18.8	28.0	13.0
TAED	-	1.0	-	5.0	-	-
AOBS	3.0	-	-	-	-	0.5
TAHD	-	-	2.0	-	4.0	-
Sodium perborate tetrahydrate	32.0	22.0	10.0	20.0	15.0	30.0
Sodium carboxymethyl cellulose	0.8	0.5	0.8	0.8	0.8	0.8
Silicone prill	2.0	-	2.0	2.0	-	2.0
EDTA	-	0.2	-	0.2	-	0.2
TlAE_{11}	0.5	2.0	-	0.5	-	0.5
Gantrez AN139	1.5	-	-	-	0.5	-
Wax	-	-	0.3	0.3	0.5	-
Gantrez AN119	-	1.0	-	1.0	0.5	1.0
Empicryl	-	-	0.5	-	-	-
Dequest 2040	-	0.2	0.5	-	1.0	1.0
Dequest 2060	0.1	-	-	0.5	-	-
Enzyme	0.3	0.3	1.0	-	0.4	-
Water & Miscellaneous	TO 100%					

The above products provide good cleaning and whiteness maintenance performance at both low and high wash temperatures on both synthetic and natural fabrics.

In the above examples, the copolymer is replaced by an equal weight of a copolymer of acrylic acid and maleic acid having a molecular weight of about 70,000 and an acrylic/maleic mole ratio of about 3:1 (Examples VII to XII.) The products again provide good cleaning and whiteness maintenance performance at both low and high wash temperatures on both synthetic and natural fabrics.

CLAIMS

1. A granular detergent composition characterized by

(a) from 2% to 35% of organic surfactant selected from anionic, nonionic, amphoteric and zwitterinoic surfactants and mixtures thereof,

(b) from 5% to 90% of phosphate detergency builder comprising at least 6% thereof of a mixture of water-soluble orthophosphate and pyrophosphate salts in a weight ratio of from 3:7 to 1:20,

(c) from 0.5% to 20% of organic peroxy acid bleach precursor, and

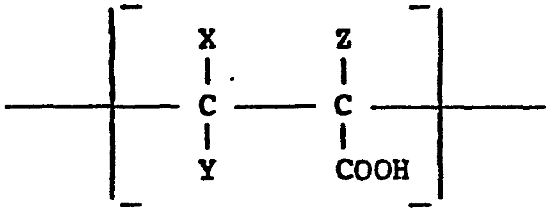
(d) from 0.1% to 2% of a homo- or copolymeric polycarboxylic acid, or salt thereof, wherein the polycarboxylic acid comprises at least two carboxyl radicals separated from one another by not more than two carbon atoms.

2. A composition according to Claim 1 characterized in that the phosphate detergency builder comprises from 50% to 90% thereof of water-soluble tripolyphosphate salts and from 10% to 50% thereof of the mixture of water-soluble orthophosphate and pyrophosphate salts.

3. A composition according to Claim 1 or 2 comprising phosphorus in an amount not exceeding that contained in 28% anhydrous sodium tripolyphosphate.

4. A composition according to any of Claims 1 to 3 characterized in that the polymeric polycarboxylic acid has an average molecular weight in the range from 500 to 2,000,000 and is a coplymer comprising

(a) polycarboxylic acid units having the general formula I

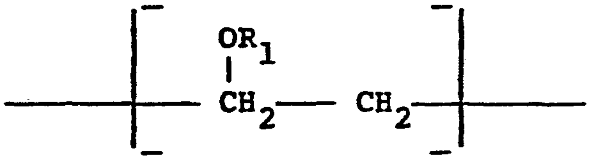


$$\left[\begin{array}{c} \\ -\!\!- \end{array}\!\!\begin{array}{c} X \\ | \\ C \\ | \\ Y \end{array}\!\!-\!\!-\!\!\begin{array}{c} Z \\ | \\ C \\ | \\ COOH \end{array}\!\!\begin{array}{c} \\ -\!\!- \end{array}\right] \qquad \text{I}$$

wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, aryl, alkaryl, carboxyl, hydroxy 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 carboxy-methyl only when Z is selected from carboxyl and carboxy-methyl and wherein only one of X, Y, and Z can be methyl, aryl, hydroxyl and alkaryl, and

(b) monomer units selected from

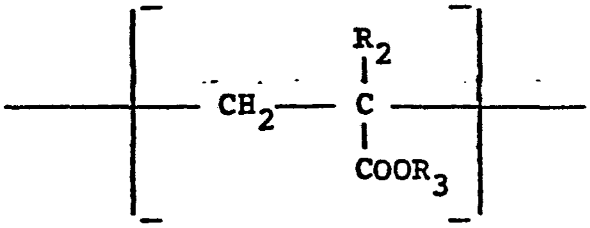
(a)



$$\left[\begin{array}{c} OR_1 \\ | \\ CH_2 \end{array}\!\!-\!\!-\, CH_2\right] \qquad \text{II}$$

wherein R_1 is a C_1 to C_{12} alkyl group or a C_1 to C_{12} acyl group, optionally being hydroxy substituted,

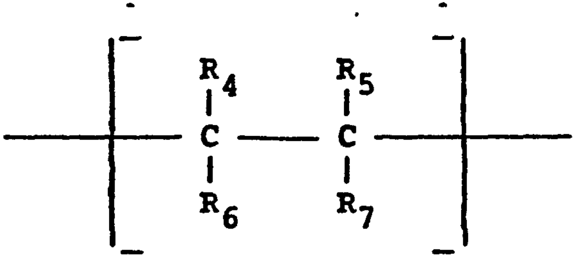
(b)



$$\left[CH_2 -\!\!- \begin{array}{c} R_2 \\ | \\ C \\ | \\ COOR_3 \end{array}\right] \qquad \text{III}$$

wherein R_2 is H or CH_3 and R_3 is H, or a C_1 to C_{10} alkyl group, R_2, R_3 optionally being hydroxy substituted,

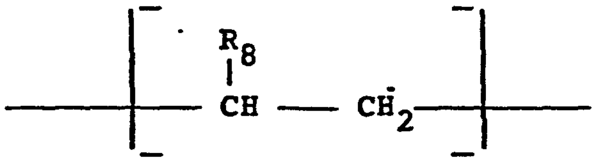
(c)



$$\left[-\overset{R_4}{\underset{R_6}{C}}-\overset{R_5}{\underset{R_7}{C}}- \right] \quad IV$$

wherein each of R_4 to R_7 is H or an alkyl group such that R_4 to R_7 together have from 1 to 20 carbon atoms, R_4 to R_7 each optionally being hydroxy substituted, and

(d)



$$\left[-\overset{R_8}{CH}-CH_2- \right] \quad V$$

in which R_8 is benzyl or pyrrolidone.

5. A composition according to Claim 4 characterized in that the polymeric polycarboxylic acid is a copolymer of maleic acid or maleic anhydride with methyl vinyl ether or ethyl vinyl ether, or acrylic acid having an average molecular weight in the range from 12,000 to 1,500,000.

6. A composition according to any of Claims 1 to 5 characterized in that the weight ratio of organic peroxy acid bleach precursor to polymeric polycarboxylic acid is from 10:1 to 1:3.

7. A composition according to any of Claims 1 to 6 characterized in that the organic peroxy acid bleach precursor is a peracetic acid bleach precursor.

8. A composition according to any of Claims 1 to 7 characterized by from 5% to 35% of a peroxy salt bleaching agent.

9. A composition according to any of Claims 1 to 8 characterized by from 0.05% to 0.2%, based on weight of magnesium, of a water-soluble magnesium salt.

10. A composition according to any of Claims 1 to 9 characterized by from 0.05% to 0.4% (acid basis) of ethylenediaminetetra(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid) or salts thereof.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 82 30 1776

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Y	BE-A- 848 034 (PROCTER & GAMBLE) *Page 8, lines 26-32; claims* ---	1,4	C 11 D 3/395 C 11 D 3/06 C 11 D 3/37
Y	GB-A-1 596 756 (PROCTER & GAMBLE) *Page 12, lines 6-8; examples; claims* ---	1,4	
A	GB-A-1 460 893 (UNILEVER) *The whole document* ---	1	
A	EP-A-0 009 954 (UNILEVER) *The whole document* -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 11 D 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-07-1982	GOLLER P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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