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(54) Title: DETERGENT COMPOSITIONS

(57) Abstract

There is provided a detergent composition adapted for use in machine dishwashing providing reduced tendency to damage glassware containing sodium silicate at a level (measured as SiO_2) of from 1 % to 11 % by weight wherein said composition has a pH measured as a 1 % solution in distilled water at 20 °C of from 9.0 to 11.5. Preferably, the composition contains a silver growth inhibitor component. When the composition contains an oxygen-releasing bleach system it also preferably contains an Mn(II) compound to reduce the propensity for silver tarnishing to occur.

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DETERGENT COMPOSITIONS

Technical Field

The present invention relates to detergent compositions, adapted for use in machine dishwashing. The compositions exhibit good bleachable stain removal, reduced propensity to damage glassware and in a highly preferred execution enhanced anti silver-tarnishing properties.

Background of the Invention

Compositions designed for use in automatic dishwasher machines are well known, and a consistent effort has been made by detergent manufacturers to improve the cleaning and/or rinsing efficiency of said compositions on dishes and glassware, as reflected by numerous patent publications.

The present invention is concerned with the formulation of a detergent composition useful in machine dishwashing having good stain removal capability, but reduced propensity to tarnish silverware and/or damage glassware.

The satisfactory removal of bleachable soils such as tea and coloured vegetable soils, such as carotenoid soils is a particular challenge to the formulator of a machine dishwashing detergent composition. Traditionally, the removal of such soils has been enabled by the use of bleach components such as oxygen and chlorine bleaches. Oxygen bleaching species are these days however, largely preferred over chlorine bleaches.

A problem encountered with the use of such oxygen bleaches is the tarnishing of any silverware components of the washload. The level of tarnishing observed can range from slight discolouration of the silverware to the formation of a dense black coating on the surface of the silverware.

There is teaching in the art, particularly German Patent Application DE-A-4,128,672 in the name of Henkel KgaA, of the use of strong alkaline, bleach-containing detergents to ameliorate the problem of the tarnishing of silverware in a machine dishwashing context. Compositions having a pH of 12.5 and 12.6 and containing high levels of sodium metasilicate are exemplified in this prior art document.

The Applicants have however, established that when such strong alkaline detergents, particularly those containing high levels of silicate, are employed there is a tendency for damage to occur to any glassware components of the washload. Such damage can manifest itself as iridescence or 'clouding' of the surface of the glassware giving rise to an unseemly visual appearance.

Surprisingly, it has been found that the tendency for damage to glassware to occur can be reduced when a product having a pH of from 9.0 to 11.5, and containing silicate at certain selected levels is employed. Particularly surprising is the finding that a reduced propensity to damage glassware can be achieved by the choice of such selected levels of silicate incorporation even over products containing no silicate.

The Applicants have also found that white calcium carbonate deposits have an enhanced tendency to form on the damaged surface of the

glassware, exacerbating the unseemly visual appearance of the glassware, and in the consumer's mind, the extent of the damage to the glassware. Control of such deposits has been found to be effectively enabled by the use of certain crystal growth inhibitor components, particularly organo diphosphonate components.

It has been found that a reduced propensity to give rise to silver tarnishing as well as good cleaning performance can be achieved through the use of certain Mn(II) compounds in oxygen bleach containing formulations. Such reduced propensity to cause silver tarnishing can be achieved by the addition of said Mn(II) compounds to non-strongly alkaline detergents.

In particular, the Applicants have found that by formulating a product having a pH of from 9.0 to 11.5 containing the aforementioned selected levels of silicate and an Mn(II) compound both good glasscare and a reduced tendency to tarnish silverware can be achieved.

To provide further reduction of silver tarnishing it has been found that the total level of oxygen bleach in the composition is desirably optimized, and preferably the rate of release of the oxygen bleach is controlled. The rate of release of oxygen bleach is preferably rapid enough to provide satisfactory cleaning, but with minimised tarnishing. In particular, the rate of release of any peroxide species to the wash solution is preferably controlled.

Compositions containing Mn(II) salts such as $MnSO_4$ and $MnCl_2$ in combination with inorganic perhydrate salts and certain bleach activators are disclosed in the aforementioned German Patent Application DE-A-4,128,672. There is no recognition provided therein of the utility of such Mn(II) salts in reducing silver tarnishing. By contrast, teaching is provided in DE-A-4,128,672 that where Mn(II) salts are used as activators for peroxy compounds there is no protection of the silver.

It is a particular object of the present invention to provide compositions, adapted for use in machine dishwashing methods, having enhanced glasscare and anti-silver tarnishing properties, as well as good cleaning performance, particularly bleachable soil removal performance.

European Patent Applications EP-A-0082563, EP-A-127,910, EP-A-141,470, EP-A-145,090 and EP-A-145,091 in the name of Unilever disclose detergent compositions for use in fabric washing containing various Mn(II) compounds. The combination of these various Mn(II) compounds with N-acylated lactam, perbenzoic acid, perbenzoic acid derivative or cationic peroxyacid precursors is not specifically disclosed. Problems specific to the art field of machine dishwashing, in particular the tarnishing of silverware, are not addressed.

European Patent Application EP-A-0 530 870 in the name of Unilever discloses machine dishwashing compositions containing a dinuclear manganese complex in which the manganese is in the III or IV oxidation state. No recognition is provided in this document of the utility of Mn (II) salts in reducing silver tarnishing.

Summary of the Invention

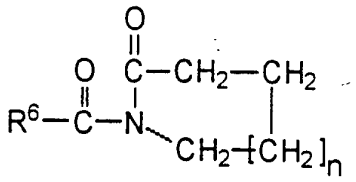
According to one aspect of the present invention there is provided a detergent composition adapted for use in a machine diswashing method containing a water soluble alkali metal silicate at a level (measured as SiO_2) of from 1% to 11% by weight wherein said composition has a pH measured as a 1% solution in distilled water at 20°C of from 9.0 to 11.5.

Preferably the detergent composition additionally contains a crystal growth inhibitor component.

Preferably the detergent composition contains

(a) an oxygen-releasing bleach system comprising a hydrogen peroxide source and a peroxyacid bleach precursor compound preferably selected from the group consisting of

(i) an N-acylated lactam bleach precursor of the formula:



wherein n is from 0 to about 8, preferably from 0 to about 2, and R^6 is H, an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons, or a substituted phenyl group containing from about 6 to about 18 carbon atoms;

(ii) a perbenzoic acid precursor

(iii) a perbenzoic acid derivative precursor

(iv) a cationic peroxyacid precursor

and any combinations of (i) - (iv); and

(b) an Mn(II) compound

Preferably, said oxygen-releasing bleaching system is incorporated such that the level of available oxygen measured according to the method herein is from 0.3% to 2.5%, preferably 0.5% to 1.7% by weight.

Preferably, the rate of release of said available oxygen is such that the available oxygen is completely released from the composition in a time interval of from 3.5 minutes to 10.0 minutes, using the test protocol described in the present description.

Preferably the bleaching composition contains no additional corrosion inhibitor component, particularly no benzotriazole.

Preferably, the Mn(II) compound is an Mn(II) salt or complex with an organic ligand, which may itself have heavy metal ion sequestering or preferably crystal growth inhibiting properties.

Detailed Description of the Invention

Machine dishwashing compositions

The compositions herein are adapted for use in a machine dishwashing method. Such compositions are formulated to enable the removal of, typically food based, soils and stains from soiled tableware under the conditions present in a machine dishwasher. Typically the compositions are low foaming, preferably containing only low levels of low-foaming surfactants.

Alkali metal silicate

The present compositions contain a water soluble alkali metal silicate. Preferred are the water soluble sodium silicates with an SiO_2: Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The alkali metal silicate may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2: Na_2O ratio of 2.0 is the most preferred silicate.

The alkali metal silicate is present in the detergent compositions in accord with the invention at a level (measured as SiO_2) of from 1% to 11%, preferably from 5% to 10%, most preferably from 6% to 9% by weight.

pH of the compositions

In an essential aspect the present compositions have a pH measured as a 1% solution in distilled water of from 9.0 to 11.5, preferably from 9.5 to 11.0, most preferably from 9.7 to 10.8.

Crystal growth inhibitor component

The detergent compositions preferably contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 1% by weight of the compositions.

By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

The organo diphosphonic acid is preferably a C_1-C_4 diphosphonic acid, more preferably a C_2 diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

Bleach system having reduced propensity to tarnish silverware

The present compositions most preferably contain an oxygen-releasing bleach system and an Mn(II) compound. The level of available oxygen is preferably controlled. Preferably, the rate of release of available oxygen and of any peroxide bleaching species is also controlled.

Oxygen-releasing bleaching system

A highly preferred feature of the invention is an oxygen-releasing bleaching system. In a preferred aspect the bleaching system comprises a hydrogen peroxide source and a peroxyacid bleach precursor compound. The production of the peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Suitable sources of hydrogen peroxide include inorganic perhydrate bleaches.

The peroxyacid bleach precursor is preferably selected from perbenzoic acid precursors, perbenzoic acid derivative precursors, N-acylated lactam bleach precursors and cationic peroxyacid precursors, or mixtures thereof.

Peroxyacid bleach precursor

The peroxyacid bleach precursors are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the compositions.

N-acylated precursor compounds of the lactam class are disclosed generally in
GB-A-855735. Whilst the broadest aspect of the invention contemplates the use of any lactam useful as a peroxyacid precursor, preferred materials comprise the caprolactams and valerolactams.

Suitable peroxyacid bleach precursors typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789.

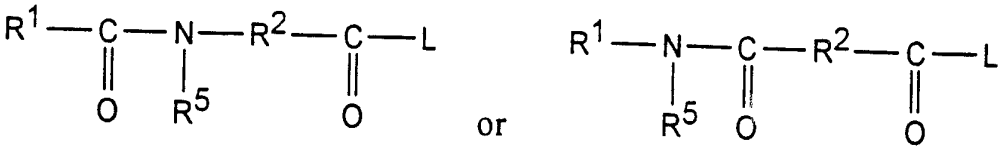
Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Useful N-acyl compounds are disclosed in GB-A-855735, 907356 and GB-A-1246338.

Preferred precursor compounds of the imide type include the N-,N,N^{1}N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Suitable imidazoles include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing peroxyacid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

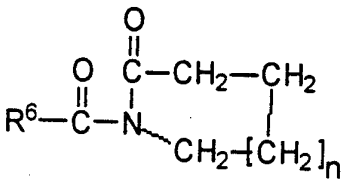
Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. L may be selected from any of the leaving groups described hereinbefore for the analogues having R^1 as an aryl or alkaryl group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

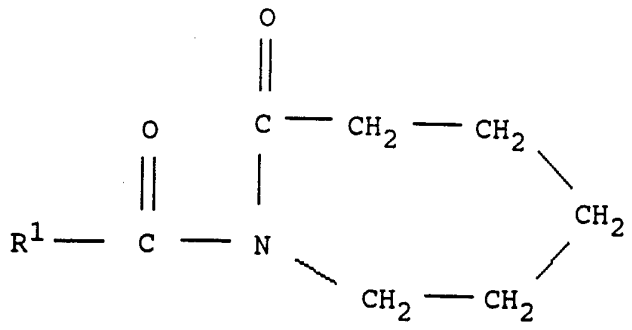
N-acylated lactam precursor

Suitable N-acylated lactam precursors have the formula:



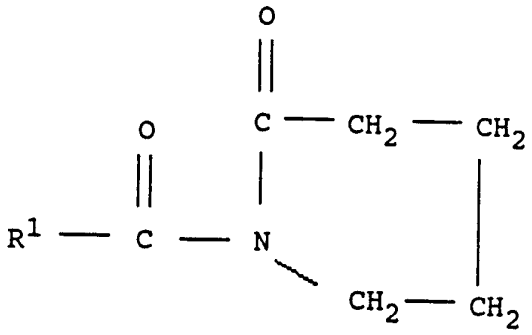
wherein n is from 0 to about 8, preferably from 0 to 2, and R^6 is H, an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons, or a substituted phenyl group containing from 6 to 18 carbon atoms

Suitable caprolactam bleach precursors are of the formula:



wherein R^1 is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms, most preferably R^1 is phenyl.

Suitable valero lactams have the formula:



wherein R^1 is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R^1 is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

The most preferred materials are those which are normally solid at <30°C, particularly the phenyl derivatives, i.e. benzoyl valerolactam, benzoyl caprolactam and their substituted benzoyl analogues such as chloro, amino alkyl, alkyl, aryl and alkoxy derivatives.

Caprolactam and valerolactam precursor materials wherein the R^1 moiety contains at least 6, preferably from 6 to 12, carbon atoms provide

peroxyacids on perhydrolysis of a hydrophobic character which afford nucleophilic and body soil clean-up. Precursor compounds wherein R^1 comprises from 1 to 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of 'hydrophobic' and 'hydrophilic' caprolactams and valero lactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

Highly preferred caprolactam and valerolactam precursors include benzoyl caprolactam, nonanoyl capro-lactam, benzoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl caprolactam, 3,5,5-trimethylhexanoyl valerolactam, octanoyl caprolactam, octanoyl valerolactam, decanoyl caprolactam, decanoyl valerolactam, undecenoyl caprolactam, undecenoyl valerolactam, (6-octanamidocaproyl)oxybenzene-sulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)-oxybenzenesulfonate, and mixtures thereof. Examples of highly preferred substituted benzoyl lactams include methylbenzoyl caprolactam, methylbenzoyl valerolactam, ethylbenzoyl caprolactam, ethylbenzoyl valerolactam, propylbenzoyl caprolactam, propylbenzoyl valerolactam, isopropylbenzoyl caprolactam, isopropylbenzoyl valerolactam, butylbenzoyl caprolactam, butylbenzoyl valerolactam, tert-butylbenzoyl caprolactam, tert-butylbenzoyl valerolactam, pentylbenzoyl caprolactam, pentylbenzoyl valerolactam, hexylbenzoyl caprolactam, hexylbenzoyl valerolactam, ethoxybenzoyl caprolactam, ethoxybenzoyl valerolactam, propoxybenzoyl caprolactam, propoxybenzoyl valerolactam, isopropoxybenzoyl caprolactam, isopropoxybenzoyl valerolactam, butoxybenzoyl caprolactam, butoxybenzoyl valerolactam, tert-butoxybenzoyl caprolactam, tert-butoxybenzoyl valerolactam, pentoxybenzoyl caprolactam, pentoxybenzoyl valerolactam, hexoxybenzoyl caprolactam, hexoxybenzoyl valerolactam, 2,4,6-trichlorobenzoyl caprolactam, 2,4,6-trichlorobenzoyl valerolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl caprolactam, dimethoxybenzoyl caprolactam, 4-chlorobenzoyl caprolactam, 2,4-dichlororbenzoyl caprolactam, terephthaloyl dicaprolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl valerolactam,

dimethoxybenzoyl valerolactam, 4-chlorobenzoyl valerolactam, 2,4-dichlororbenzoyl valerolactam, terephthaloyl divalerolactam, 4-nitrobenzoyl caprolactam, 4-nitrobenzoyl valerolactam, and mixtures thereof.

Perbenzoic acid precursor

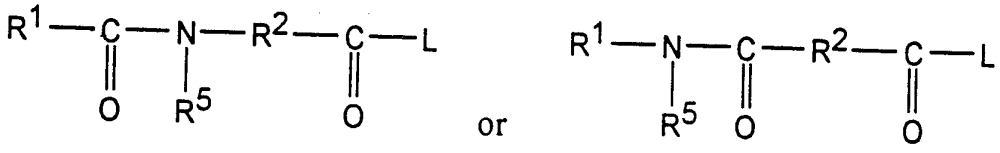
Essentially any perbenzoic acid precursors are suitable herein, including those of the N-acylated lactam class, which are preferred.

Specific O-acylated perbenzoic acid precursor compounds include benzoyl oxybenzene sulfonate and monobenzoyltetraacetyl glucose benzoyl peroxide.

Preferred perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas.

Preferred perbenzoic acid precursors include the benzoyl diacyl peroxides and benzoyl tetraacyl peroxides.

Another preferred class of perbenzoic acid precursor compounds are the amide substituted compounds of the following general formulae:

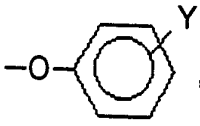
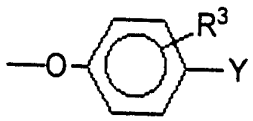
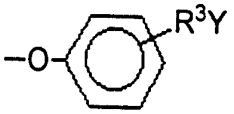


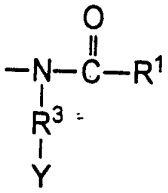
wherein R^1 is an aryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be aryl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include

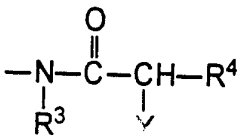
alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

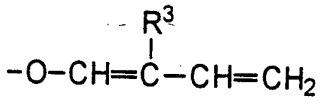
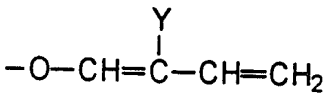
The L group must be sufficiently reactive for the reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. These characteristics are generally paralleled by the pKa of the conjugate acid of the leaving group, although exceptions to this convention are known. Ordinarily, leaving groups that exhibit such behaviour are those in which their conjugate acid has a pKa in the range of from 4 to 13, preferably from 6 to 11 and most preferably from 8 to 11.

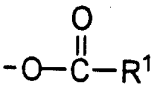
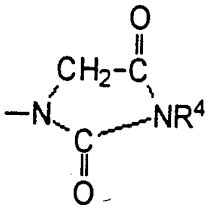
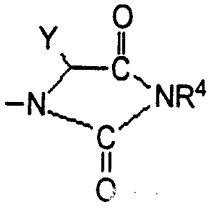
Preferred bleach precursors are those wherein R^1, R^2 and R^5 are as defined for the amide substituted compounds and L is selected from the group consisting of:

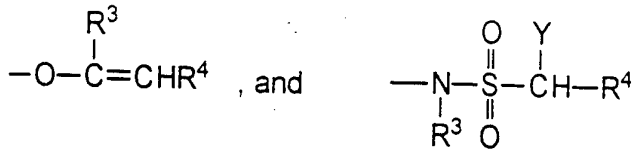

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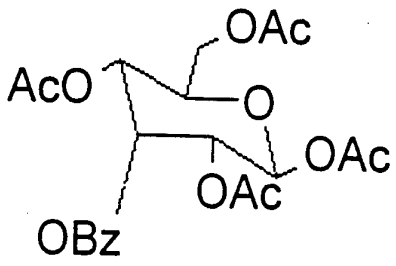
and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group.

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<--N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing groups should be well dispersed in the bleaching solution in order to assist in their dissolution.

Other preferred perbenzoic acid precursors include:

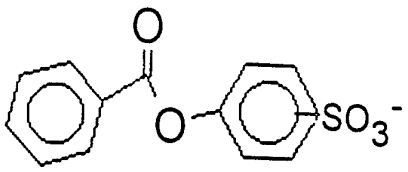
Benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents.

Example : Ac = COCH3; Bz = Benzoyl

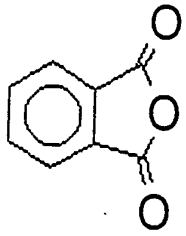


Mono Benzoyltetraacetyl Glucose.

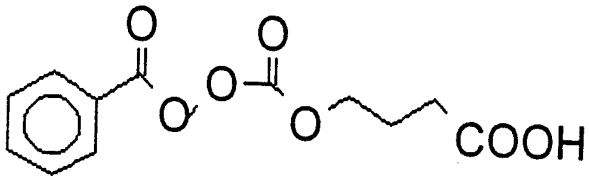
BOBS:



Phthalic anhydride:



Preformed peracids including:



Perbenzoic acid derivative precursors

Suitable perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the perbenzoic group is substituted by essentially any functional group including alkyl groups.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds are also suitable herein. Typically such cationic peroxyacid precursors are formed by substituting the peroxyacid part with an ammonium or alkyl ammmonium group, preferably an ethyl or methyl ammonium group.

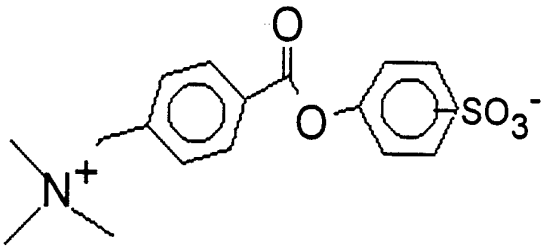
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022;

5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and copending US Patent Applications having the Procter & Gamble attorneys' docket No's 5410, 5411, 5412 and 5413.

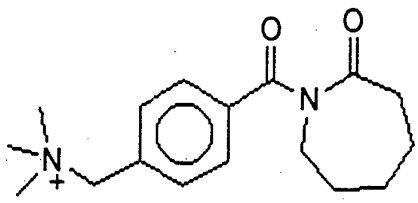
Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:



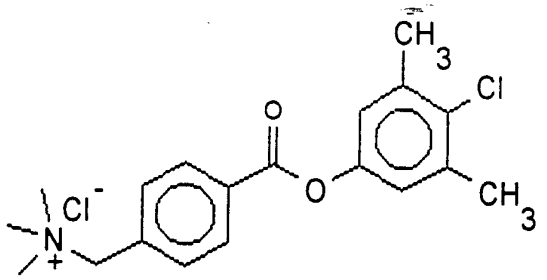
A preferred cationically substituted alkyl oxybenzene sulfonate is the methyl ammonium derivative of 2,3,3-tri-methyl hexanoyloxybenzene sulfonate.

Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:

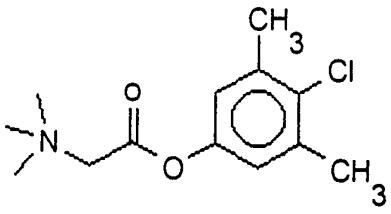


Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

Also preferred is trimethyl ammonium methylene meta chloro xylenol:



Betaine ester trimethyl ammonium meta chloro xylenol is also preferred:



Inorganic perhydrate bleaches

The compositions in accord with the invention include a hydrogen peroxide source. Suitable hydrogen peroxide sources include the inorganic perhydrate salts.

The inorganic perhydrate salts are normally incorporated in the form of the sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which

provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Sodium percarbonate, which is a preferred perhydrate for inclusion in compositions in accordance with the invention, is an addition compound having a formula typically corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in product stability.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4.n.Na_2CO_3$ wherein n is form 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

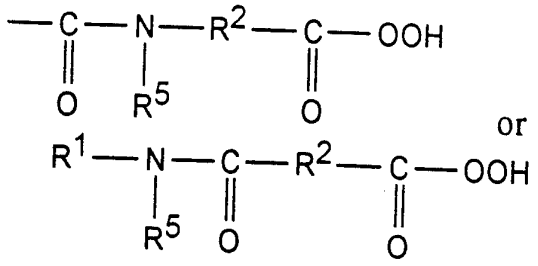
Other coatings which contain silicate (alone or with borate salts or boric acids or other inorganics), waxes, oils, fatty soaps can also be used advantageously within the present invention.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Organic peroxyacids

The compositions may also contain organic peroxyacids, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diperoxydodecanedioc acid, diperoxytetradecanedioc acid, diperoxyhexadecanedioc acid, mono- and diperazelaic acid, mono- and diperbrassylic acid, monoperoxy phthalic acid and its magnesium salt, perbenzoic acid, and their salts as disclosed in, for example, EP-A-0341 947.

Total Available Oxygen (AvO) Level

It has been found that, for optimal anti-silver tarnishing performance, the level of available oxygen in the present compositions, measured in units of % available oxygen by weight of the composition, should preferably be carefully controlled; the level of available oxygen should hence preferably

be in the range from 0.3% to 2.5%, preferably from 0.5% to 1.7%, more preferably from 0.6% to 1.5%, most preferably from 0.7% to 1.2%, measured according to the method described hereunder.

Rate of Release of AvO

The rate of release of available oxygen is preferably also controlled; the rate of release of available oxygen from the compositions herein preferably should be such that, when using the method described hereinafter, the available oxygen is not completely released from the composition until after 3.5 minutes, preferably the available oxygen is released in a time interval of from 3.5 minutes to 10.0 minutes, more preferably from 4.0 minutes to 9.0 minutes, most preferably from 5.0 minutes to 8.5 minutes.

Method for Measuring Level of Total Available Oxygen (AvO) and Rate of Release of AvO in a Detergent Composition

Method

1. A beaker of water (typically 2L) is placed on a stirrer Hotplate, and the stirrer speed is selected to ensure that the product is evenly dispersed through the solution.

2. The detergent composition (typically 8g of product which has been sampled down from a bulk supply using a Pascal sampler), is added and simultaneously a stop clock is started.

3. The temperature control should be adjusted so as to maintain a constant temperature of 20°C throughout the experiment.

4. Samples are taken from the detergent solution at 2 minute time intervals for 20 minutes, starting after 1 minute, and are titrated by the "titration procedure" described below to determine the level of available oxygen at each point.

Titration Procedure

1. An aliquot from the detergent solution (above) and 2ml sulphuric acid are added into a stirred beaker

2. Approximately 0.2g ammonium molybdate catalyst (tetra hydrate form) are added

3. 3mls of 10% sodium iodide solution are added

4. Titration with sodium thiosulphate is conducted until the end point. The end point can be seen using either of two procedures. First procedure consists simply in seeing the yellow iodine colour fading to clear. The second and preferred procedure consists of adding soluble starch when the yellow colour is becoming faint, turning the solution blue. More thiosulphate is added until the end point is reached (blue starch complex is decolourised).

The level of AvO, measured in units of % available oxygen by weight, for the sample at each time interval corresponds to the amount of titre according to the following equation

$$\frac{\text{Vol } S_2O_3(\text{ml}) \times \text{Molarity } (S_2O_3) \times 8}{\text{Sample mass (g)}}$$

AvO level is plotted versus time to determine the maximum level of AvO, and the rate of release of AvO

Rate of release of organic peroxyacid

The rate of release of any organic peroxyacid species is also preferably controlled. The kinetics of release to a wash solution are preferably such that in the T50 test method herein described the time to achieve a concentration that is 50% of the ultimate concentration of the peroxyacid

bleach is from 180 seconds to 480 seconds, more preferably from 200 seconds to 400 seconds, most preferably from 240 seconds to 360 seconds.

Rate of release of organic peroxyacid - test method

The controlled release kinetics or organic peroxyacid herein are defined with respect to a 'TA test method' which measures the time to achieve A% of the ultimate concentration/level of the organic peroxyacid when a composition containing the organic peroxyacid is dissolved according to the standard conditions now set out.

The standard conditions involve a 1 litre glass beaker filled with 1000 ml of distilled water at 20°C, to which 10g of composition is added. The contents of the beaker are agitated using a magnetic stirrer set at 100 rpm. The ultimate concentration/level is taken to be the concentration/level maximum level of organic peroxyacid attained after addition of the composition to the water-filled beaker.

Suitable analytical methods are chosen to enable a reliable determination of the incidental, and ultimate in solution concentrations of the organic peroxyacid, subsequent to the addition of the composition to the water in the beaker.

Such analytical methods can include those involving a continuous monitoring of the level of concentration of the component, including for example photometric and conductrimetric methods.

Alternatively, methods involving removing titres from the solution at set time intervals, stopping the dissolution process by an appropriate means such as by rapidly reducing the temperature of the titre, and then determining the concentration of the component in the titre by any means such as chemical titrimetric methods, can be employed.

Suitable graphical methods, including curve fitting methods, can be employed, where appropriate, to enable calculation of the TA value from raw analytical results.

The particular analytical method selected for determining the concentration of the organic peroxyacid component, will depend on the nature of that component, and of the nature of the composition containing that component.

Controlled rate of release - means

A means may be provided for controlling the rate of release of oxygen bleach to the wash solution.

Means for controlling the rate of release of the bleach may provide for controlled release of peroxide species to the wash solution. Such means could, for example, include controlling the release of any inorganic perhydrate salt, acting as a hydrogen peroxide source, to the wash solution.

Suitable controlled release means can include coating any suitable component with a coating designed to provide the controlled release. The coating may therefore, for example, comprise a poorly water soluble material, or be a coating of sufficient thickness that the kinetics of dissolution of the thick coating provide the controlled rate of release.

The coating material may be applied using various methods. Any coating material is typically present at a weight ratio of coating material to bleach of from 1:99 to 1:2, preferably from 1:49 to 1:9.

Suitable coating materials include triglycerides (e.g. partially) hydrogenated vegetable oil, soy bean oil, cotton seed oil) mono or diglycerides, microcrystalline waxes, gelatin, cellulose, fatty acids and any mixtures thereof.

Other suitable coating materials can comprise the alkali and alkaline earth metal sulphates, silicates and carbonates, including calcium carbonate and silicas.

A preferred coating material particularly for an inorganic perhydrate salt bleach source is sodium silicate of SiO_2 : Na_2O ratio from 1.6 : 1 to 3.4 : 1, preferably 2.2:1 to 2.8:1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the inorganic perhydrate salt. Magnesium silicate can also be included in the coating.

Any inorganic salt coating materials may be combined with organic binder materials to provide composite inorganic salt/organic binder coatings. Suitable binders include the C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole of alcohol and more preferably the C_{15}-C_{20} primary alcohol ethoxylates containing from 20 - 100 moles of ethylene oxide per mole of alcohol.

Other preferred binders include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols (PEG) with an average molecular weight of from 600 to 5 x 10^6 preferably 1000 to 400,000 most preferably 1000 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole. Further examples of binders include the C_{10}-C_{20} mono- and diglycerol ethers and also the C_{10}-C_{20} fatty acids.

Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts are other examples of binders suitable for use herein.

One method for applying the coating material involves agglomeration. Preferred agglomeration processes include the use of any of the organic binder materials described hereinabove. Any conventional agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Molten coating compositions may also

be applied either by being poured onto, or spray atomized onto a moving bed of bleaching agent.

Other means of providing the required controlled release include mechanical means for altering the physical characteristics of the bleach to control its solubility and rate of release. Suitable protocols could include compaction, mechanical injection, manual injection, and adjustment of the solubility of the bleach compound by selection of particle size of any particulate component.

Whilst the choice of particle size will depend both on the composition of the particulate component, and the desire to meet the desired controlled release kinetics, it is desirable that the particle size should be more than 500 micrometers, preferably having an average particle diameter of from 800 to 1200 micrometers.

Additional protocols for providing the means of controlled release include the suitable choice of any other components of the detergent composition matrix such that when the composition is introduced to the wash solution the ionic strength environment therein provided enables the required controlled release kinetics to be achieved.

Mn (II) compound

The compositions most preferably contain an Mn(II) compound to inhibit the tarnishing of silverware. The Mn(II) compound is preferably incorporated at a level of from 0.005% to 5% by weight, more preferably from 0.01% to 1%, most preferably from 0.02% to 0.4% by weight of the compositions. Preferably, the Mn(II) compound is incorporated at a level to provide from 0.1 ppm to 250 ppm, more preferably from 0.5 ppm to 50 ppm, most preferably from 1 ppm to 20 ppm by weight of Mn(II) ions in any bleaching solution.

The Mn (II) compound may be an inorganic salt in anhydrous, or any hydrated forms. Suitable salts include manganese sulphate, manganese carbonate, manganese phosphate, manganese nitrate, manganese acetate and manganese chloride.

The Mn(II) compound may be a salt or complex of an organic fatty acid such as manganese acetate or manganese stearate.

The Mn(II) compound may be a salt or complex of an organic ligand. Preferably any salts/complexes are water soluble. In one preferred execution the organic ligand is a heavy metal ion sequestrant. In another preferred execution the organic ligand is a crystal growth inhibitor component.

By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Suitable heavy metal ion sequestrants include organic amniophosphonates, such as the amino alkylene poly (alkylene phosphonates), and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) and hexamethylene diamine tetra (methylene phosphonate).

Other suitable heavy metal ion sequestrants include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid, and the partially or fully ionized forms thereof. Ethylenediamine disuccinic acid is preferred, most preferably in the form of its S,S isomer.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β-

alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based heavy metal ion sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS) is also suitable.

The organic ligand may be a crystal growth inhibitor component, particularly an organo diphosphonic acid component as described hereinbefore.

Optional Ingredients

In addition to the essential ingredients described hereinabove, the compositions of the invention may comprise additional ingredients, which are often quite desirable ones.

Water-soluble builder compound

The compositions of the present invention may contain as a highly preferred component a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, carbonates, bicarbonates, borates, phosphates, and mixtures of any of the foregoing.

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

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. 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 No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 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 No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, 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, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

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

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less that about 50°C, especially less than about 40°C.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Partially soluble or insoluble builder compound

The compositions of the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of partially water soluble builders include the crystalline layered silicates. Examples of largely water insoluble builders include the sodium aluminosilicates.

Crystalline layered sodium silicates have the general formula

$$NaMSi_xO_{2x+1}.yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. The most preferred material is δ-$Na_2Si_2O_5$, available from Hoechst AG as NaSKS-6.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof.

Suitable aluminosilicate zeolites have the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]$. XH_2O wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate ion exchange materials can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeoilte MAP, Zeolite HS and mixtures thereof. Zeolite A has the formula

$Na_{12}[AlO_2)_{12}(SiO_2)_{12}]. xH_2O$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]. 276\ H_2O$.

Surfactant

A highly preferred component of the compositions of the invention is a surfactant system comprising surfactant selected from anionic, cationic,

nonionic ampholytic and zwitterionic surfactants and mixtures thereof. Preferably the surfactant system comprises low foaming surfactant, which is typically nonionic in character. The surfactant system is typically present at a level of from 0.2% to 30% by weight, more preferably from 0.5% to 10% by weight, most preferably from 1% to 5% by weight of the compositions.

A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31,1981. A listing of surfactants typically included in automatic dishwashing detergent compositions is given in EP-A-0414 549.

Sulphonate and sulphate surfactants are useful herein. Sulphonates include alkyl benzene sulphonates having from 5 to 15 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid testers in which the fatty acid is derived from a C_6-C18 fatty source. Preferred sulphate surfactants are alkyl sulphates having from 6 to 16, preferably 6 to 10 carbon atoms in the alkyl radical.

Useful surfactant system comprises a mixture of two alkyl sulphate materials whose respective mean chain lengths differ from each other. The cation in each instance is again an alkali metal, preferably sodium.The alkyl sulfate salts may be derived from natural or synthetic hydrocarbon sources.

The C_6-C_{16} alkyl ethoxysulfate salt comprises a primary alkyl ethoxysulfate which is derived from the condensation product of a C_6-C_{16} alcohol condensed with an average of from one to seven ethylene oxide groups, per mole. Preferred are the C_6-C_{10} alkyl ethoxysulfate salts with an average of from one to five ethoxy groups per mole.

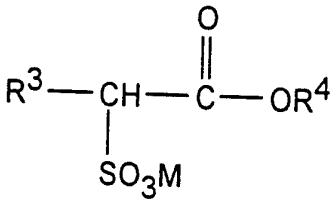
Other anionic surfactants suitable for the purposes of the invention are the alkali metal sarcosinates of formula

$$R\text{-}CON\ (R^1)\ CH_2\ COOM$$

wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the lauroyl, Cocoyl (C_{12}-C_{14}), myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

Another class of anionic surfactants useful herein are the alkyl ester sulfonate surfactants which include linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society," 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactants have the structural formula:



wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl, and $R^4$is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10}-C_{16} alkyl.

One preferred class of low foaming nonionic surfactants useful in the present invention comprises the water soluble ethoxylated C_6-C_{16} fatty alcohols and C_6-C_{16} mixed ethoxylated/propoxylated fatty alcohols and mixtures thereof. Preferably the ethoxylated fatty alcohols are the C_{10}-C_{16} ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C_{12}-C_{16} ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed

ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

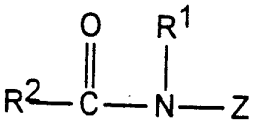
Thus C6-C16 alcohol itself can be obtained from natural or synthetic sources. Thus, C6-C16 alcohols, derived from natural fats, or Ziegler olefin build-up, or OXO synthesis can form suitable sources for the alkyl group. Examples of synthetically derived materials include Dobanol 25 (RTM) sold by Shell Chemicals (UK) Ltd which is a blend of C_{12}-C_{15} alcohols, Ethyl 24 sold by the Ethyl Corporation which is a blend of C_{12}-C_{15} alcohols, and a blend of C_{13}-C_{15} alcohols in the ratio 67% C_{13}, 33% C_{15} sold under the trade name Lutensol by BASF GmbH and Synperonic (RTM) by ICI Ltd., and Lial 125 sold by Liquichimica Italiana. Examples of naturally occuring materials from which the alcohols can be derived are coconut oil and palm kernel oil and the corresponding fatty acids.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula

$$RO\ (C_nH_{2n}O)_tZ_x$$

wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 6 to 16 carbon atoms preferably from 6 to 14 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

Another preferred nonionic surfactant is a polyhydroxy fatty acid amide surfactant compound having the structural formula:



wherein R^1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (ie., methyl); and R^2 is a C_5-C_{15} hydrocarbyl, preferably straight chain C_5-C_{13} alkyl or alkenyl, more preferably straight chain C_5-C_{11} alkyl or alkenyl, most preferably straight chain C_5-C_9 alkyl or alkenyl, or mixture thereof: and Z is a polyhydroxyhydrocarbyl having linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxlylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)-CH_2OH$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly - $CH_2-(CHOH)_4-CH_2OH$.

In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

R^2-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, or tallowamide.

Z can be 1-deoxyglucityl, 2-deoxyfrucittyl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl or 1-deoxymannityl, or 1-deoxymalto-triotityl. Preferred compounds are N-methyl N-1deoxyglucityl C_{14}-C_{18} fatty acid amides.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C_6-C_{20}, preferably C_6-C_{10} N-alkyl or alkenyl amine oxides and propylene-1,3-

diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxpropyl groups.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Heavy metal ion sequestrant

The compositions may contain narrowly defined levels of a heavy metal ion sequestrant which is not in the form of a Mn(II) compound, such levels being in the range 0.005% to 3%, preferably 0.01 to 1%, most preferably 0.05% to 0.8%, by weight of the total composition.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable non Mn(II) counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

The heavy metal ion sequestrant may be any of those described as suitable heavy metal ion sequestrant-type organic ligands in the Mn(II) compounds section of this description.

Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_3EDDS. Examples of such preferred magnesium complexes of EDDS include MgEDDS and Mg_2EDDS.

The heavy metal ion sequestrant herein can consist of a mixture of the above described species.

Optional chlorine bleach components

Chlorine bleaches include the alkali metal hypochlorites and chlorinated cyanuric acid salts. The use of chlorine bleaches in the composition of the invention is optional and preferably minimized, and more preferably the present compositions contain no chlorine bleach.

Enzyme

Another optional ingredient useful in the compositions is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme (lipase) may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein.

A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Enzyme Stabilizing System

Preferred enzyme-containing compositions herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%,most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, and mixtures thereof. Such stabilizing systems can also comprise reversible enzyme inhibitors, such as reversible protease inhibitors.

The compositions herein may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially

under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during washing is usually large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are widely available, and are illustrated by salts containing ammonium cations or sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc. and mixtures thereof can be used if desired.

Organic polymeric compound

Organic polymeric compounds are particularly preferred components of the compositions in accord with the invention. By organic polymeric compound it is meant essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of molecular

weight 2000-10000 and their copolymers with any suitable other monomer units including modified acrylic, fumaric, maleic, itaconic, aconitic, mesaconic, citraconic and methylenemalonic acid or their salts, maleic anhydride, acrylamide, alkylene, vinylmethyl ether, styrene and any mixtures thereof. Preferred are the copolymers of acrylic acid and maleic anhydride having a molecular weight of from 20,000 to 100,000.

Preferred commercially available acrylic acid containing polymers having a molecular weight below 15,000 include those sold under the tradename Sokalan PA30, PA20, PA15, PA10 and Sokalan CP10 by BASF GmbH, and those sold under the tradename Acusol 45N by Rohm and Haas.

Preferred acrylic acid containing copolymers include those which contain as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula -[CR_2-CR_1(CO-O-R_3)]- wherein at least one of the substituents R_1, R_2 or R_3, preferably R_1 or R_2 is a 1 to 4 carbon alkyl or hydroxyalkyl group, R_1 or R_2 can be a hydrogen and R_3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_1 is methyl, R_2 is hydrogen (i.e. a methacrylic acid monomer). The most preferred copolymer of this type has a molecular weight of 3500 and contains 60% to 80% by weight of acrylic acid and 40% to 20% by weight of methacrylic acid.

Other suitable polyacrylate/modified polyacrylate copolymers include those copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents No.s 4,530,766, and 5,084,535 which have a molecular weight of less than 15,000.

Other suitable organic polymeric compounds include the copolymers of acrylamide and acrylate having a molecular weight of from 3,000 to 100,000, and the acrylate/fumarate copolymers having a molecular weight of from 2,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Lime soap dispersant compound

The compositions of the invention may contain a lime soap dispersant compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap dispersant compound is preferably present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. A numerical measure of the effectiveness of a lime soap dispersant is given by the lime soap dispersing power (LSDP) which is determined using the lime soap dispersion test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to , for example, in the following review articles; W.N. Linfield, Surfactant Science Series, Volume 7, p3; W.N. Linfield, Tenside Surf. Det. , Volume 27, pages159-161, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm $CaCO_3$ (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap dispersant capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the invention include C_{16}-C_{18} dimethyl amine oxide, C_{12}-C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12}-C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of about 3 (LSDP=4), and the C_{13}-C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the trade names Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap dispersants suitable for use herein are described in the article by M.K. Nagarajan and W.F. Masler, to be found in Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). Examples of such polymeric lime soap dispersants include certain water-soluble salts of copolymers of acrylic acid, methacrylic acid or mixtures thereof, and an acrylamide or substituted acrylamide, where such polymers typically have a molecular weight of from 5,000 to 20,000.

Suds suppressing system

The compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl and alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressors typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

Copolymers of ethylene oxide and propylene oxide, particularly the mixed ethoxylated/propoxylated fatty alcohols with an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10, are also suitable antifoam compounds for use herein.

Suitable 2-alky-alcanols antifoam compounds for use herein have been described in DE 40 21 265. The 2-alkyl-alcanols suitable for use herein consist of a C_6 to C_{16} alkyl chain carrying a terminal hydroxy group, and said alkyl chain is substituted in the a position by a C_1 to C_{10} alkyl chain. Mixtures of 2-alkyl-alcanols can be used in the compositions according to the present invention.

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C_{16}-C_{18} ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A preferred particulate suds suppressor system useful herein comprises a mixture of an alkylated siloxane of the type hereinabove disclosed and solid silica.

The solid silica can be a fumed silica, a precipitated silica or a silica, made by the gel formation technique. The silica particles suitable have an average particle size of from 0.1 to 50 micrometers, preferably from 1 to 20 micrometers and a surface area of at least $50m^2/g$. These silica particles can be rendered hydrophobic by treating them with dialkylsilyl groups and/or trialkylsilyl groups either bonded directly onto the silica or by means of a silicone resin. It is preferred to employ a silica the particles of which have been rendered hydrophobic with dimethyl and/or trimethyl silyl groups. A preferred particulate antifoam compound for inclusion in the detergent compositions in accordance with the invention suitably contain an amount of silica such that the weight ratio of silica to silicone lies in the range from 1:100 to 3:10, preferably from 1:50 to 1:7.

Another suitable particulate suds suppressing system is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above $50m^2/g$, 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.

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Other highly preferred particulate suds suppressing systems are described in copending European Application 91870007.1 in the name of the

Procter and Gamble Company which systems comprise silicone antifoam compound, a carrier material, an organic coating material and glycerol at a weight ratio of glycerol : silicone antifoam compound of 1:2 to 3:1. Copending European Application 91201342.0 also discloses highly preferred particulate suds suppressing systems comprising silicone antifoam compound, a carrier material, an organic coating material and crystalline or amorphous aluminosilicate at a weight ratio of aluminosilicate : silicone antifoam compound of 1:3 to 3:1. The preferred carrrier material in both of the above described highly preferred granular suds controlling agents is starch.

An exemplary particulate suds suppressing system for use herein is a particulate agglomerate component, made by an agglomeration process, comprising in combination

(i) from 5% to 30%, preferably from 8% to 15% by weight of the component of silicone antifoam compound, preferably comprising in combination polydimethyl siloxane and silica;

(ii) from 50% to 90%, preferably from 60% to 80% by weight of the component, of carrier material, preferably starch;

(iii) from 5% to 30%, preferably from 10% to 20% by weight of the component of agglomerate binder compound, where herein such compound can be any compound, or mixtures thereof typically employed as binders for agglomerates, most preferably said agglomerate binder compound comprises a C_{16}-C_{18} ethoxylated alcohol with a degree of ethoxylation of from 50 to 100; and

(iv) from 2% to 15%, preferably from 3% to 10%, by weight of C_{12}-C_{22} hydrogenated fatty acid.

Polymeric dye transfer inhibiting agents

The compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

Additional corrosion inhibitor

The compositions may contain, but preferably do not contain, additional corrosion inhibitor inhibitors such as benzotriazole and paraffin.

Form of the compositions

The compositions of the invention can be formulated in any desirable form such as powders, granulates, pastes, liquids, gels and tablets, granular forms being preferred.

The bulk density of the granular detergent compositions in accordance with the present invention is typically of at least 650 g/litre, more usually at least 700 g/litre and more preferably from 800 g/litre to 1200 g/litre.

Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrial cup disposed below the funnel. The funnel is 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement e.g. a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide the bulk density in g/litre. Replicate measurements are made as required.

The particle size of the components of granular compositions in accordance with the invention should preferably be such that no more that 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

Generally, if the compositions are in liquid form the liquid should be thixotropic (ie; exhibit high viscosity when subjected to low stress and lower viscosity when subjected to high stress), or at least have very high viscosity, for example, of from 1,000 to 10,000,000 centipoise. In many cases it is desirable to include a viscosity control agent or a thixotropic agent to provide a suitable liquid product form. Suitable thixotropic or viscosity control agents include methyl cellulose, carboxymethylcellulose, starch, polyvinyl, pyrrolidone, gelatin, colloidal silica, and natural or synthetic clay minerals.

Pasty compositions in accordance with the invention generally have viscosities of about 5,000 centipoise and up to several hundred million centipoise. In order to provide satisfactory pasty compositions a small amount of a solvent or solubilizing agent or of a gel-forming agent can be included. Most commonly, water is used in this context and forms the continuous phase of a concentrated dispersion. Certain nonionic surfactants at high levels form a gel in the presence of small amount of water and other solvents. Such gelled compositions also envisaged in the present invention.

Washing method

Any suitable methods for washing or cleaning soiled tableware, including soiled glassware and silverware, are envisaged including machine dishwashing methods.

Machine dishwashing method

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous liquid having dissolved or

dispensed therein an effective amount of a machine dishwashing composition in accord with the inevntion. By an effective amount of the machine dishwashing composition it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

In the detergent compositions, the abbreviated component identifications have the following meanings:

XYEZS	:	C_{1X} - C_{1Y} sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole
Nonionic	:	C_{13}-C_{15} mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF Gmbh (low foaming)
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O ratio = 2.0)
Carbonate	:	Anhydrous sodium carbonate
Phosphate	:	Sodium tripolyphosphate
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000
AA	:	Polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH
Citrate	:	Tri-sodium citrate dihydrate

PB1	:	Anydrous sodium perborate monohydrate
PB4	:	Anhydrous sodium perborate tetrahydrate
Percarbonate	:	Anhydrous sodium percarbonate bleach of empirical formula $2Na_2CO_3.3H_2O_2$ coated with a mixed salt of formula $Na_2SO_4.n.Na_2CO_3$ where n is 0.29 and where the weight ratio of percarbonate to mixed salt is 39:1
TAED	:	Tetraacetyl ethylene diamine
BOBS	:	Benzoyloxybenzenesulfonate
Caprolactam	:	Benzoylcaprolactam
Paraffin	:	Paraffin oil sold under the tradename Winog 70 by Wintershall.
Protease	:	Proteolytic enzyme sold under the tradename Savinase by Novo Industries A/S (approx 2% enzyme activity).
Alcalase	:	Proteolytic enzyme sold by Novo Industries A/S under the tradename Alcalase 2T (approximately 2% enzyme activity)
Amylase	:	Amylolytic enzyme sold under the tradename Termamyl 60T by Novo Industries A/S (approx 0.9% enzyme activity)
Lipase	:	Lipolytic enzyme sold under the tradename Lipolase by Novo Industries A/S (approx 2% enzyme activity)

DETPMP	:	Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
Granular Suds Suppressor	:	12% Silicone/silica, 18% stearyl alcohol,70% starch in granular form
Sulphate	:	Anhydrous sodium sulphate.
pH	:	Measured as a 1% solution in distilled water at 20°C.

In the following examples all levels of enzyme quoted are expressed as % active enzyme by weight of the composition.

Example 1

The following machine dishwashing detergent compositions were prepared (parts by weight). Composition A is a prior art composition, compositions B to F are in accord with the invention.

	A	B	C	D	E	F
Citrate	37.3	37.3	37.3	-	1.25	10.0
Citric Acid	-	-	-	18.6	17.5	11.0
MA/AA	3.7	3.7	3.7	6.0	6.0	6.0
Silicate (as SiO_2)	17.0	5.0	6.0	8.5	8.5	8.5
Carbonate	-	-	-	4.5	15.5	-
Bicarbonate	-	-	-	-	-	20.0
Percarbonate	-	-	-	10.4	-	-
PB1	10.4	10.4	10.4	-	10.4	10.4
TAED	3.0	3.0	3.0	3.0	3.0	4.4
Caprolactam	-	-	-	3.8	-	3.8
BOBS	-	-	-	-	3.8	-
Protease	0.04	0.04	0.04	-	-	-
Amylase	0.02	0.02	0.02	0.03	0.03	0.03

Alcalase	-	-	-	0.07	0.07	0.07
DETPMP	-	-	-	0.13	0.13	0.13
Nonionic	1.5	1.5	1.5	-	2.0	3.0
Sulphate	2.0	22.0	20.0	12.1	12.1	12.1
35AE3S	-	-	-	3.0	-	-
Granular Suds Suppressor	-	-	-	2.0	-	-
misc/moisture to balance						
pH (1% solution)	10.7	10.3	*8.5	8.5	9.0	9.0

* The pH was adjusted, as necessary, by addition of H_2SO_4 as a pH trim.

Comparative testing 1

The following comparative glasscare testing was conducted; compositions B and C of Example I were compared for glasscare performance, to a reference composition (composition A of Example I).

The testing involved complete immersion of six clear glass beakers in a 1% product solution of each of compositions A to C at 65°C for 168 hours. This test is believed to be representative of the conditions which would be experienced in 504 complete 20 minute wash cycles in a machine dishwasher.

Performance was graded by 4 expert panellists through visual inspection according to a scale of from 2 to 10 where:

10 = as new
2 = severe iridescence and clouding

Results were as follows : (average of the 4 gradings from the panellists)

Composition A	Composition B	Composition B
2.0	9.3	9.8

Example 2

The following base machine dishwashing detergent compositions were prepared (parts by weight).

	A	B	C	D	E	F
Citrate	15.0	15.0	-	24.0	24.0	29.0
Phosphate	-	-	46.0	-	-	-
MA/AA	-	-	-		6.0	-
AA	6.0	6.0	-	6.0	-	-
Silicate (as SiO_2)	10.0	9.0	10.0	6.0	6.0	6.0
Carbonate	20.0	20.0	15.0	15.0	15.0	15.0
Percarbonate	9.1	9.1	9.1	9.1	9.1	1.9
PB4	-	-	-	-	-	8.7
Caprolactam	7.0	6.0	8.0	7.0	6.0	4.4
Total AvO	1.2	1.2	1.2	1.2	1.2	1.2
Benzotriazole	0.5	0.4	0.6	-	0.5	0.3
Paraffin	0.5	0.5	-	0.6	0.5	0.5
Protease	0.04	0.03	0.03	0.04	0.04	0.04
Amylase	0.02	0.01	0.01	0.02	0.01	0.01

Lipase	-	-	0.03	0.03	0.03	-
DETPMP	0.13	-	-	-	-	0.5
HEDP	0.5	0.5	0.5	0.5	0.5	0.5
Nonionic	1.5	1.7	1.5	1.5	1.5	1.5
Sulphate	1.4	2.4	2.4	12.1	12.1	3.0
35AE3S	-	-	5.0	-	5.0	-
Granular Suds Suppressor	-	-	1.0	-	1.0	-
misc/moisture to balance						
pH	10.5	10.5	10.5	10.0	10.0	10.0

To each of base compositions A to F the following Mn(II) compounds were added at the indicated levels to give compositions in accord with the invention.

Mn(II) compound	Level of addition (by weight)
Mn(II) SO_4	0.1
$MnCl_2$	0.1
Mn(II) HEDP	0.13
Mn(II) EDDS	0.13
Mn(II) DETPMP	0.13

Comparative testing 1

The following comparative testing was conducted; base composition A of Example I was compared for anti-silver tarnishing performance to reference compositions G and H containing 0.13% $MnSO_4$ and 0.13% Mn(II)EDDS respectively.

The testing involved machine testing, using a Bosch Siemens dishwasher, 20g product dosage, 65°C economy cycles, and 14 cycles.

Silver tarnishing performance was graded by 4 expert panellists through visual inspection according to the following scale :

where 0 = no tarnish (shiny silver)
1 = very slight tarnish
2 = tarnish
3 = very tarnished
4 = severe tarnish (black coverage)

Results were as follows : (average of the 4 gradings from the panellists)

Composition A	Composition B	Composition C
2.0	<0.5	<0.5

Composition A also showed a satisfactory glasscare profile in accord with the invention.

CLAIMS

1. A detergent composition adapted for use in a machine dishwashing method containing a water soluble alkali metal silicate at a level (measured as SiO_2) of from 1% to 11% by weight wherein said composition has a pH measured as a 1% solution in distilled water at 20°C of from 9.0 to 11.5.

2. A detergent composition according to Claim 1 containing said water soluble alkali metal silicate at a level (measured as SiO_2) of from 6% to 9% by weight wherein said composition has a pH as a 1% solution in distilled water of 20°C of from 9.5 to 11.0.

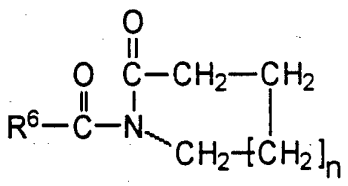
3. A detergent composition according to either of Claims 1 or 2 containing a crystal growth inhibitor component.

4. A detergent composition according to any of Claims 1 - 3 containing

(a) an oxygen-releasing bleach system comprising a hydrogen peroxide source and a peroxyacid bleach precursor compound; and

(b) an Mn(II) compound

5. A detergent composition according to Claim 4 wherein said peroxyacid precursor compound is selected from the group consisting of



wherein n is from 0 to about 8, preferably from 0 to about 2, and R^6 is H, an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons, or a substituted phenyl group containing from about 6 to about 18 carbon atoms;

(ii) a perbenzoic acid precursor

(iii) a perbenzoic acid derivative precursor

(iv) a cationic peroxyacid precursor

and any combinations of (i) - (iv)

6. A detergent composition according to either of Claims 4 or 5 wherein said Mn(II) compound is an Mn(II) salt or complex with an organic ligand.

7. A detergent composition according to Claim 6 wherein said organic ligand has heavy metal ion sequestering properties.

8. A detergent composition according to Claim 7 wherein said organic ligand is ethylenediamine disuccinic acid.

9. A bleaching composition according to Claim 6 wherein said organic ligand has crystal growth inhibiting properties.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/12405

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 3/08, 3/395, 7/54, 9/42; C01B 15/00
US CL : 252/94, 95, 97, 135, 186.33
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/94, 95, 97, 135, 186.33

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 3,850,832 (WEGEMUND ET AL) 26 November 1974, Example 6 in Table I; col. 4 line 57 to col. 5 line 46	1-3
X	US, A, 4,430,243 (BRAGG) 07 February 1984, abstract; col. 2 line 65 to col. 3 line 4, 46-50; Examples II, V, VIII and IX in cols. 14-15	1-3
X	US, A, 4,515,704 (AKRED ET AL) 07 May 1985, Examples 3-4, 7-10, 19, 26, 28-30, 33-34, 45-46, 51-52, 56-59, 63-64 and 66; col. 19 lines 19-23	1-3
X	US, A, 4,623,357 (URBAN) 18 November 1986, abstract; Examples 56-57 in Table V	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 06 FEBRUARY 1995	Date of mailing of the international search report 13 FEB 1995
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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/12405

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-9
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS, STN
search terms: dishwashing, (sodium or alkali metal)silicate#, crystal growth inhibitor#, diphosphonic acid, hedp, bleach catalyst#, bleach precursor#, caprolactam, valerolactam, ethylenediamine disuccinic acid