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(54) Automatic dishwashing composition containing bleach activators.

(57) Automatic dishwashing detergent compositions comprising a peroxygen bleaching compound and a bleach activator are disclosed. The bleach activators are selected from the group consisting of benzoyloxybenzenesulphonate (BOBS), benzoylcaprolactam (BZCL), benzoylvalerolactam (BZVL), nonanoyloxybenzenesulphonate (NOBS), derivatives and mixtures thereof. Preferred compositions are granular, are substantially phosphate free and contain detersive enzymes. The compositions are effective in removing tea stains under various temperature and pH conditions.

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TECHNICAL FIELD

The present invention is in the field of automatic dishwashing detergents. More specifically, the invention relates to granular automatic dishwashing detergents which provide enhanced cleaning and glass care benefits. The automatic dishwashing compositions comprise a peroxygen bleach component and a oxybenzene sulfonate, valerolactam, and/or caprolactam, particularly valerolactum or caprolactam, type bleach activator at a wash solution pH of at least 8.

BACKGROUND OF THE INVENTION

Automatic dishwashing detergents (hereinafter ADDs) used for washing tableware in the home or institutionally in machines especially designed for the purpose have long been known. Dishwashing in the seventies is reviewed by Mizuno in Vol. 5, Part III of the Surfactant Science Series, Ed. W.G. Cutler and R.C. Davis, Marcel Dekker, N.Y., 1973, incorporated by reference. The particular requirements of cleansing tableware and leaving it in a sanitary, essentially spotless, residue-free state has indeed resulted in so many particular ADD compositions that the body of art pertaining thereto is now recognized as quite distinct from other cleansing product arts.

In light of legislation and current environmental trends, modern ADD products desirably contain low levels or are substantially free of inorganic phosphate builder salts and/or are concentrated formulations (i.e. 1/2 cup vs. full cup usage). Unfortunately, nonphosphated ADD products in technical terms may sacrifice efficacy, especially owing to the deletion of phosphate and, in some instances, chlorine mainstay cleansing ingredients. Concentrated or compact compositions similarly exhibit formulation problems.

Users of ADDs have come to expect tableware will be rendered essentially spotless and film-free in addition to cleaning. In practice, this means avoiding film-forming components. The formulator must employ ingredients which are sufficiently soluble that residues or build-up do not occur. Again, while some ingredients may be adequate on grounds of cleaning, spotting and filming, solubility considerations may diminish their usefulness. Solubility considerations are even more acute with the newer "low usage", "concentrated", ADD compositions whose overall solubility can be less than that of conventional ("full cup") products.

It has generally been believed by the formulator of ADDs that inexpensive cleaning can be achieved via high alkalinity and/or high silicate levels (for example as provided by formulations comprising high percentages by weight of sodium hydroxide or metasilicate). It has been discovered that severe penalties result in these compositions in terms of product corrosiveness to dishwashers and tableware, especially china and glassware and incompatibility with other detergent ingredients. It is therefore highly desirable, at least in some phosphate-free compact ADDs, to achieve good cleaning end-results without resorting to the use of high alkalinity/high silicate.

Peroxygen bleaches are effective for stain and/or soil removal, but such bleaches are temperature and/or pH dependent. As a consequence, there has been a substantial amount of research to develop bleaching systems which contain an activator that renders peroxyygen bleaches effective in various wash liquor conditions.

A widely-used bleach activator in ADDs is tetraacetyl ethylene diamine (TAED). TAED provides some hydrophilic cleaning expecially food and beverage stains, but there are problems associated with its use, i.e. plow to release and solubility in efficiency. It has now unexpectedly been discovered that automatic dishwashing detergents, preferably granular or powder-form, can be provided with improved cleaning and glasscare benefits by formulating selected peroxygen bleach compounds with oxybenzene sulfonate, valerolactam and/or caprolactam activators, preferably valerolactam or caprolactam activators, into the ADDs. These ADD formulations have particularly defined pH ranges and bleach (AvO) to bleach activator ratios. The composition when dissolved at from about 2000 to about 6000 ppm (parts per million) preferably from about 2500 to about 4500 ppm in an automatic dishwasher affords a pH in the range from about 8 to about 13, more preferably from about 9 to about 12, even more preferably from about 9.5 to about 11.5. The molar ratio of bleach (AvO) to bleach activator is at least 1:1, preferably from about 20:1 to about 1:1, more preferably from about 10:1 to about 3:1.

In addition it has been determined that some bleaching systems, particularly those comprising a dihydrophobic bleach activator (i.e. TAED) and a source of hydrogen peroxide, the bleach activator undergoes perhydrolysis to form a peroxyacid bleaching agent. A by-product of the perhydrolysis reaction between such bleach activators and hydrogen peroxide is a diacylperoxide (DAP) species. It has now further been discovered that the DAP's derived from hydrophobic activators tend to be insoluble, poorly dispersible, oily materials which form a residue which can deposit on the natural rubber machine parts that are exposed to the wash liquor. The oily DAP residue can form a film on the natural rubber parts and promote free radical and peroxide damage to the rubber, which eventually leads to failure of the part. This is particularly true of rubber parts which have prolonged exposure to the wash liquor.

By the present invention, it has now been discovered that the class of bleach activators derived from caprolactams and valerolactams form peroxyacids upon perhydrolysis without the production of oily, harmful DAP's. Without intending to be bound by theory, it is believed that these bleach activators provide good cleaning performance with safety to natural rubber, since they do not expose the natural rubber machine parts or articles to DAP oxidation. Whatever the reason, natural rubber parts and articles remain substantially undamaged by the bleaching systems of the present invention.

It has also been surprisingly found that oxybenzene sulphonate or valerolactam bleach activators are especially efficient in ADD formulations at pH wash solution ranges from about 8 to about 9.5.

The novel ADDs have the property of removing stains, especially tea stains, and tough food objected to by the consumer from dishware, even in a low, i.e. mildly alkaline, pH. The compositions have other cleaning and spotlessness advantages such as enhanced glass care (i.e. reduction of cloudiness and iridescence negatives) and reduction of silicate/carbonate deposition filming negatives. ADD embodiments including phosphate free compositions and enzyme-containing compositions are provided for powerful cleaning of wide-ranging soils while retaining the advantages of a generally mild and noncorrosive product matrix.

SUMMARY OF THE INVENTION

The present invention encompasses automatic dishwashing detergent compositions, especially granular or powder-form automatic dishwashing detergent compositions, comprising by weight

(a) from about 0.01% to about 8%, preferably 0.1 to about 5%, more preferably from about 0.3% to about 4%, most preferably from about 0.8% to about 3% (as AvO) of peroxygen bleach selected from the group consisting of percarbonate, perborate, monopersulfate and mixtures thereof;

(b) from about 0.01% to about 15%, preferably from about 1% to about 10%, more preferably from about 0.1% to about 8%, of bleach activator selected from the group comprising benzoyloxybenzenesulphonate (BOBS), benzoylcaprolactam (BZCL), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C_8-COBS), nonanoyloxybenzenesulphonate (NOBS), phenylbenzoate (PhBz), eptaolyoxybenzenesulphonate (C_{10}-OBS) derivatives; and mixtures thereof; and

(c) from about 0.1% to about 50%, preferably from about 5% to about 30%, of pH adjusting components, said component providing a wash solution pH from about 8 to about 13, preferably from about 9 to about 12;

wherein a molar ration of component (a) to component (b) is from about 20:1 to about 1:1, preferably from about 10:1 to about 3:1.

While peroxygen bleach compounds, activator and suitable pH agents are the essential ingredients to the present invention, there are also provided embodiments wherein additional components, especially silicate, enzymes and/or nonionic surfactant are desirably present. Highly preferred embodiments of the invention are substantially free from phosphate salts and have low (e.g., < 15% SiO_2) total silicate content. Additional components include but are not limited to suds suppressors, other detergent surfactants and mixtures thereof.

The present invention also encompasses a method for cleaning soiled tableware comprising contacting said tableware with an aqueous medium having a pH in the range from about 8 to about 13, more preferably from about 9 to about 12, and comprising at least from about 0.01% to about 8% (as AvO) of a peroxygen bleach selected from the group consisting of percarbonate, perborate, persulfate and mixtures thereof; and from about 0.01% to about 15% bleach acitivator selected from the group consisting of benzoyloxybenzenesulphonate (BOBS), benzoylcaprolactam (BZCL), benzoylvalerolactam (BZVL) octanoyloxybenzenesulphonate (C_8-OBS), nonanoyloxybenzenesulphonate (NOBS), phenylbenzoate (PhBz) heptaoyloxybenzenesulphonate (C_{10}-OBS), derivatives; and mixtures thereof. The essential peroxygen bleach component, activator and pH adjusting agents are added in a solid form to an automatic dishwashing machine.

DETAILED DESCRIPTION OF THE INVENTION

An automatic dishwashing detergent composition comprising by weight:

a) from about 0.01% to about 8% (as AvO) of a peroxygen bleach selected from the group consisting of percarbonate, perborate, monopersulfate and mixtures thereof;

b) from about 0.01% to about 15% of a peroxygen bleach activator selected from the group consisting of benzoyloxybenzenesulphonate (BOBS), benzoylcaprolactam (BZCL), benzoylvalerolactam (BZVL) octanoyloxybenzenesulphonate (C_8-OBS), nonanoyloxybenzenesulphonate (NOBS), phenylbenzoate (PhBz), heptaoyloxybenzenesulphonate (C_{10}OBS), derivatives; and mixtures thereof; and

c) from about 0.1% to about 50% of a pH adjusting component to provide a wash solution pH of from about 8 to about 13;

wherein said composition comprises an AvO to bleach activator ratio of at least 1:1. A particularly preferred embodiment is phosphate free and further comprises from about 0.5% to about 12%, active detersive enzyme.

The term "substantially free" herein refers to substances that are not intentionally added to the ADD but could be present as impurities in commercial grade raw materials or feedstocks. For example, the present invention encompasses substantially phosphate-free embodiments. Such embodiments generally comprise less than 0.5% of phosphate as P_2O_5.

The term "wash solution" is defined herein to mean an aqueous solution of the product dissolved at 2,000-6,000 ppm, preferably at 2,500-4,500 ppm, in an automatic dishwasher.

Peroxygen Bleach

The ADD compositions of the present invention contain an amount of oxygen bleach sufficient to provide from 0.01% to about 8%, preferably from about 0.1% to about 5.0%, more preferably from about 0.3% to about 4.0%, most preferably from about 0.8% to about 3% of available oxygen (AvO) by weight of the ADD.

Available oxygen of an ADD or a bleach component is the equivalent bleaching oxygen content thereof expressed as %O. For example, commercially available sodium perborate monohydrate typically has an available oxygen content for bleaching purposes of about 15% (theory predicts a maximum of about 16%). Methods for determining available oxygen of a formula after manufacture share similar chemical principles but depend on whether the oxygen bleach incorporated therein is a simple hydrogen peroxide source such as sodium perborate or percarbonate, is an activated type (e.g., perborate with tetra-acetyl ethylenediamine) or comprises a preformed peracid such as monoperphthalic acid. Analysis of peroxygen compounds is well-known in the art: see, for example, the publications of Swern, such as "Organic Peroxides", Vol. I, D.H. Swern, Editor; Wiley, New York, 1970, LC # 72-84965, incorporated by reference. See for example the calculation of "percent active oxygen" at page 499. This term is equivalent to the terms "available oxygen" or "percent available oxygen" as used herein.

The peroxygen bleaching systems useful herein are those capable of yielding hydrogen peroxide in an aqueous liquor. These compounds include but are not limited to the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide and inorganic persalt bleaching compounds such as the alkali metal perborates, percabonates, perphosphates, and the like. Mixtures of two or more such bleaching compounds can also be used.

Preferred peroxygen bleaching compounds include sodium perborate, commercially available in the form of mono-, tri-, and tetra-hydrate, sodium pyrophosphate peroxyhydrate, , urea peroxyhydrate, sodium percarbonate, and sodium peroxide. Particularly preferred are sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate. Percarbonate is especially preferred because of environmental issues associated with boron. Many geographies are forcing legislation to eliminate elements such as boron from formulations.

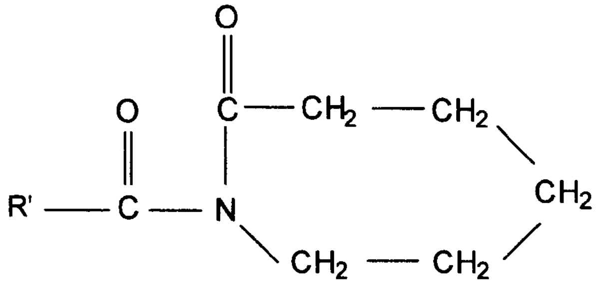
Suitable oxygen-type bleaches are further described in U.S. Patent No. 4,412,934 (Chung et al), issued November 1, 1983, and peroxyacid bleaches described in European Patent Application 033,259. Sagel et al, published September 13, 1989, both incorporated herein by reference, can be used.

Highly preferred percarbonate can be in uncoated or coated form. The average particle size of uncoated percarbonate ranges from about 400 to about 1200 microns, most preferably from about 400 to about 600 microns. If coated percarbonate is used, the preferred coating materials include carbonate, sulphate, silicate, borosilicate, fatty carboxylic acids, and mixtures thereof.

Activator

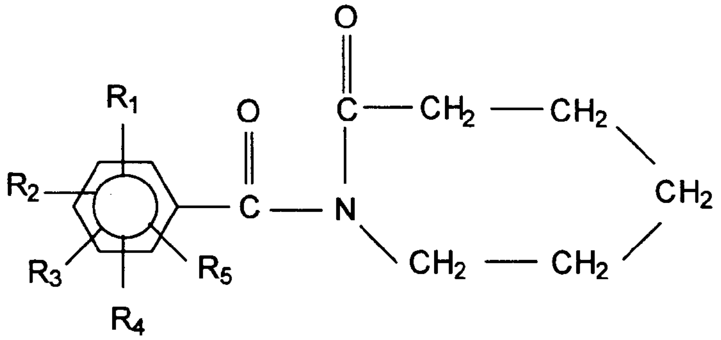
For the excellent bleaching results of the present invention the peroxygen bleach component is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01% to about 15%, preferably from about 1% to about 10%, more preferably from about 1% to about 8%, by weight of the composition. Preferred activators are selected from the group consisting of benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenylbenzoate (PhBz), heptaoyloxybenzenesulphonate (C_{10}-OBS), benzolyvalerolactam (BZVL), octanoyloxybenzenesulphonate (C_8-OBS), perhydrolyzable esters and mixtures thereof, preferably 3-chlorobenzoylcaprolactam and benzolyvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred caprolactam derived activators are of the formula:

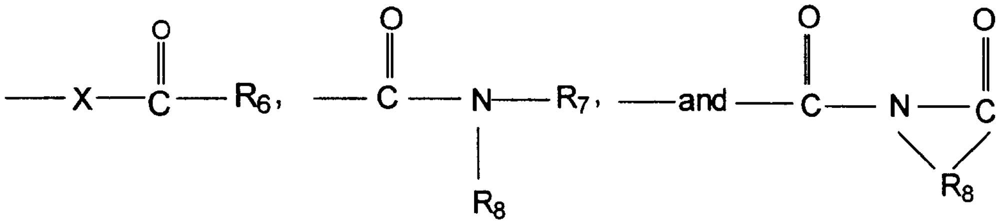


wherein R^1 is a hydrocarbyl subsituent which contains at least 6 carbon atoms.

Other perferred caprolactams have the formula:



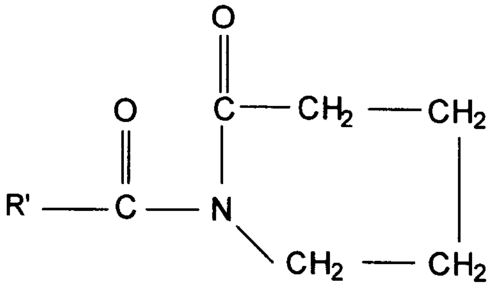
wherein R_1,R_2,R_3,R_4 and R_5 contain from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms and are members selected from the group consisting of H, halogen, alkyl, alkoxy, alkoxyaryl, arlaryl, alkaryloxy, and substituents having the structure:



wherein R_6 is selected from the group consisting of H, alkyl, alkaryl, alkoxy, alkoxyaryl, alkaryloxy, and aminoalkyl; X is 0, NH or NR_7, wherein R_7 is H or a C_1-C_4 alkyl group; and R_6 is an alkyl, cycoalkyl, or aryl group containing from 3 to 11 carbon atoms; provided that at least one R substituent is not H.

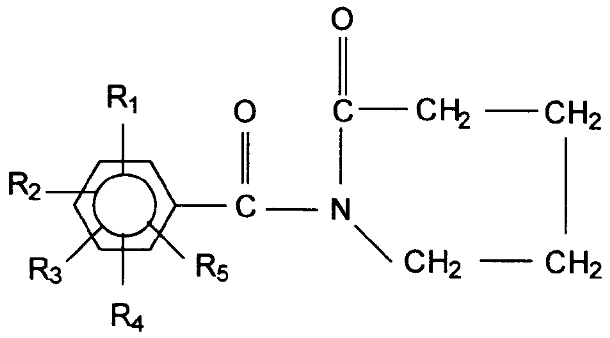
Preferred valerolactam activators are selected from the group consisting of:

i)

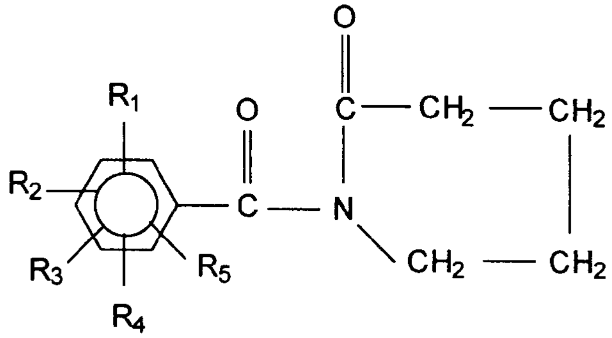


wherein R^1 is a substituted or unsubstituted, including saturated or unsaturated alkyl, or alkoxy group containing from about 1 to about 18 carbon atoms, wherein the longest linear alkylor alkoxy chain extending

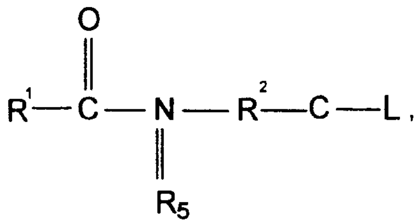
from and including the carbonyl carbon containing from about 2 to about 12 carbon atoms.
ii)



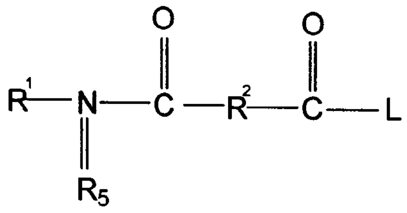
wherein R_1, R_2, R_3, R_4, and R_5 may be the same or different substituents selected from alkoxy.
iii)



Preferred Phenybenzoate activators are the general formulas:
wherein R^1 is an alkyl, aryl, or alkaryl group containing from about 1 to about 14 carbon atoms, R^2 is an alylene, arylene or alkarylene group containing from about 1 to about 14 carbon atoms, R^5 is H or an alkyl, aryl, or alkaryl group containing from about 1 to about 10 carbon atoms, and L is a leaving group, and



$$R^1-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle R_5}{\|}}{N}-R^2-C-L,$$



$$R^1-\underset{\underset{\displaystyle R_5}{\|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-R^2-\overset{\overset{\displaystyle O}{\|}}{C}-L$$

Preferred bleach activators are those described in U.S. Patent 5,130,045, Mitchell et al, and copending patent applications U. S. Serial Nos. 08/064,624, 08/064,623, 08/064,621, 08/064,562, 08/064,564, 08/082,270 and copending application to M. Burns, A.D. Willey, R.T. Hartshom, C.K. Ghosh, entitled "Bleaching Compounds Comprising Peroxyacid Activators Used With Enzymes" and having U.S. Serial No. ______________ __ (P&G Case 4890R), all of which are incorporated herein by reference.

The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1 to about 1:1, more preferably from about 10:1 to about 3:1.

pH-Adjusting Control Components

The compositions herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders. It has been discovered that to secure the benefits of the invention, the peroxygen bleaching component must at least be combined with a pH-adjusting component which delivers a wash solution pH of from 8 to about 13, preferably from about 9 to about 12, more preferably from about 9.5 to about 11.0. The pH-adjusting component are selected so that when the ADD is dissolved in water at a concentration of 2000 - 6000 ppm, the pH remains in the ranges discussed above. The preferred nonphosphate pH-adjusting component embodiments of the invention is selected from the group consisting of

(i) sodium carbonate or sesquicarbonate
(ii) sodium silicate, preferably hydrous sodium silicate having SiO_2:Na_2O ratio of from about 1.:1 to about 2:1;
(iii) sodium citrate
(iv) citric acid
(v) sodium bicarbonate
(vi) sodium borate, preferably borax
(vii) sodium hydroxide; and
(viii) mixtures of (i)-(vii).

Preferred embodiments contain low levels of silicate (i.e. less than 10% SiO_2).

Illustrative of highly preferred pH-adjusting component systems are binary mixtures of granular sodium citrate with anhydrous sodium carbonate, and three-component mixtures of granular sodium citrate trihydrate, citric acid monohydrate and anhydrous sodium bicarbonate.

The amount of the pH adjusting component in the instant ADD compositions is generally from about 0.9% to about 99%, preferably from about 1% to about 50%, by weight of the composition. In a preferred embodiment, the pH-adjusting component is present in the ADD composition in an amount from about 5% to about 40%, preferably from about 10% to about 30%, by weight.

For compositions herein having a pH between about 9.5 and about 10.5 (i.e. the inital wash solution) particularly preferred ADD embodiments comprise, by weight of ADD, from about 5% to about 40%, preferably from about 10% to about 30%, most preferably from about 15% to about 20%, of sodium citrate with from about 5% to about 30%, preferably from about 7% to 25%, most preferably from about 8% to about 20% sodium carbonate.

The essential pH-adjusting system can be complemented (i.e. for improved sequestration in hard water) by other optional detergency builder salts selected from nonphosphate detergency builders known in the art, which include the various water-soluble, alkali metal, ammonium or substituted ammonium borates, hydroxysulfonates, polyacetates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of such materials. Alternate water-soluble, non-phosphorus organic builders can be used for their sequestering properties. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, ethylenediamine disuccinic acid (especially the S,S- form); nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxymethyloxysuccinic acid, mellitic acid, and sodium benzene polycarboxylate salts.

Bleachable stain benefits can be achieved by deployment of an activator containing oxygen bleach system discussed hereinabove in a controlled pH system. The pH control system delivers a pH "jump/drop" profile wherein the pH rises quickly (i.e. within 1 minute) in the wash to an initial pH of from about 9.5 to about 13, preferably from about 9.8 to about 12, more preferably from about 9.9 to about 11. This initial pH is maintained for a sufficient period of time, preferably from about 10 seconds to about 10 minutes, more preferably from about 0.5 minutes to about 3 minutes. The initial high pH allows sufficient peracid formation via perhydrolysis of the activator(s). The initial pH is then reduced to a pH of less than about 9.5. The lower pH maximizes bleach performance and enhances glass care protection when low levels of silicate discussed herein are present.

Compositions of the present invention having a wash solution pH from about 8 to about 9.5 comprise a bleach activator selected from the group having an oxybenzene sulphonate or valerolactam leaving group.

In general, pH values of the instant compositions can vary during the course of the wash as a result of the water and soil present. The best procedure for determining whether a given composition has the herein-indicated pH values is as follows: prepare an aqueous solution or dispersion of all the ingredients of the composition by mixing them in finely divided form with the required amount of water to have a 3000 ppm total concentration. Do not have any coatings on the particles capable of inhibiting dissolution. (In the case of the second pH adjusting component it should be omitted from the formula when determining the formula's initial pH value). Measure the pH using a conventional glass electrode at ambient temperature, within about 2 minutes of forming the solution or dispersion. To be clear, this procedure relates to pH measurement and is not intended to be construed as limiting of the ADD compositions in any way; for example, it is clearly envisaged that fully-formulated embodiments of the instant ADD compositions may comprise a variety of ingredients applied as coatings to other ingredients, particularly the second pH adjusting component.

Bleach Catalyst

The bleach catalyst material used herein can comprise the free acid form, the salts, and the like.

One type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenedi-aminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

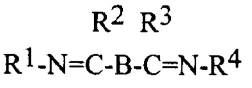
Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of theses catalysts include $Mn^{IV}_2(u\text{-}O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triacyclononane})_2\text{-}(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triacyclononane})_2\text{-}(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6(1,4,7\text{-triacyclononane})_4\text{-}(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triacyclononane})_2\text{-}(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triaza-cyclononane, and mixtures thereof.

The bleach catalysts useful in machine dishwashing compositions and concentrated powder detergent compositions may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084.

See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $Mn(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane}(OCH_3)_3\text{-}(PF_6)$.

Still another type of bleach activator, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (II), (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulsitol, mannitol, xylithol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with an non-(macro)-cyclic ligand. Said ligands are of the formula:



$$R^1\text{-}N{=}\overset{R^2}{C}\text{-}B\text{-}\overset{R^3}{C}{=}N\text{-}R^4$$

wherein R^1, R^2, R^3, and R^4 can each be selected from H, substituted alkyl and aryl groups such that each $R^1\text{-}N{=}C\text{-}R^2$ and $R^3\text{-}C{=}N\text{-}R^4$ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S. CR^5R^6, NR^7 and C=O, wherein R^5, R^6, and R^7 can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe,-bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include $Co(2,2'\text{-bispyridylamine})Cl_2$, Di(isothiocyanato)bispyridylamine-cobalt (II), trisdipyridylamine-cobalt(II) perchlorate, $Co(2,2\text{-bispyridylamine})_2O_2ClO_4$, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Other examples include Mn gluconate, $Mn(CF_3SO_3)_2$, $Co(NH_3)_5Cl$, and the binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$and $[Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2]\text{-}(ClO_4)_3$.

The bleach catalysts of the present invention may also be prepared by combining a water-soluble ligand with a water-soluble manganese salt in aqueous media and concentrating the resulting mixture by evaporation. Any convenient water-soluble salt of manganese can be used herein. Manganese (II), (III), (IV) and/or (V) is readily available on a commercial scale. In some instances, sufficient manganese may be present in the wash liquor, but, in general, it is preferred to add Mn cations in the compositions to ensure its presence in catalytically-effective amounts. Thus, the sodium salt of the ligand and a member selected from the group consisting of $MnSO_4$, $Mn(ClO_4)_2$ or $MnCl_2$ (least preferred) are dissolved in water at molar ratios of ligand:Mn ^{s}alt in the range of about 1:4 to 4:1 at neutral or slightly alkaline pH. The water may first be de-oxygenated by boiling and cooled by sparging with nitrogen. The resulting solution is evaporated (under N_2, if desired) and the resulting solids are used in the bleaching and detergent compositions herein without further purification.

In an alternate mode, the water-soluble manganese source, such as $MnSO_4$, is added to the bleach/cleaning composition or to the aqueous bleaching/cleaning bath which comprises the ligand. Some type of complex is apparently formed *in situ*, and improved bleach performance is secured. In such an *in situ* process, it is convenient to use a considerable molar excess of the ligand over the manganese, and mole ratios of ligand:Mn typically are 3:1 to 15:1. The additional ligand also serves to scavenge vagrant metal ions such as iron and copper, thereby protecting the bleach from decomposition. One possible such system is described in European patent application, publication no. 549,271.

While the structures of the bleach-catalyzing manganese complexes of the present invention have not been elucidated, it may be speculated that they comprise chelates or other hydrated coordination complexes which result from the interaction of the carboxyl and nitrogen atoms of the ligand with the manganese cation. Likewise, the oxidation state of the manganese cation during the catalytic process is not known with certainty, and may be the (+II), (+III), (+IV) or (+V) valence state. Due to the ligands' possible six points of attachment to the manganese cation, it may be reasonably speculated that multi-nuclear species and/or "cage" structures may exist in the aqueous bleaching media. Whatever the form of the active Mn ligand species which actually exists, it functions in an apparently catalytic manner to provide improved bleaching performances on stubborn stains such as tea, ketchup, coffee, blood, and the like.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Silicates

The compositions of the type described herein optionally, but preferably comprise alkali metal silicates. The alkali metal silicates hereinafter described provide pH adusting capablity, protection against corrosion of metals and against attack on dishware, inhibition of corrosion to glasswares and chinawares, the sodium silicate levels should be kept at low levels and in the presence of low pH, preferably pH from about 7 to about 9.4, more preferably from about 8.5 to about 9.3. It has been found that at final wash solutions of greater than pH 9.5 the presence of silicate (as SiO_2), especially at levels of greater than 11%, negatively impacts glasscare (i.e. glass corrosion).

Glasscare can be enhanced when the wash solution pH comprising a dissolved silicate containing ADD is less than 9.5, preferably from aout 6.5 to about 9.5, more preferably from about 7.0 to about 9.3, most preferably from about 8.0 to about 9.2. Under these conditions the SiO_2 level is from about 0.5% to about 12 %, preferably from about 1% to about 11%, more preferably from about 2% to about 10%, most preferably from about 3% to about 9%, based on the weight of the ADD. The ratio of SiO_2 to the alkali metal oxide (M_2O, where M=alkali metal) is typically from about 1 to about 3.2, preferably from about 1 to about 3, more preferably from about 1 to about 2.4. Preferably, the alkali metal silicate is hydrous, having from about 15% to about 25% water, more preferably, from about 17% to about 20%.

Anhydrous forms of the alkali metal silicates with a SiO_2:M_2O ratio of 2.0 or more are also less preferred because they tend to be significantly less soluble than the hydrous alkali metal silicates having the same ratio.

Sodium and potassium, and especially sodium, silicates are preferred. A particularly preferred alkali metal silicate is a granular hydrous sodium silicate having a SiO_2:Na_2O ratio of from 2.0 to 2.4 available from PQ Corporation, named Britesil H20 and Britesil H24. Most preferred is a granular hydrous sodium silicate having a SiO_2:Na_2O ratio of 2.0. While typical forms, i.e. powder and granular, of hydrous silicate particles are suitable, preferred silicate particles have a mean particle size between about 300 and about 900 microns with less than 40% smaller than 150 microns and less than 5% larger than 1700 microns. Particularly preferred is a silicate particle with a mean particle size between about 400 and about 700 microns with less than 20% smaller than 150 microns and less than 1% larger than 1700 microns.

Other suitable silicates include the crystalline layered sodium silicates have the general formula

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

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 s. The most preferred material is $Na_2Si_2O_5$, 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.

Low-Foaming Nonionic Surfactant

ADD compositions of the present invention can comprise low foaming nonionic surfactants (LFNIs). LFNI can be present in amounts from 0 to about 10% by weight, preferably from about 0.25% to about 4%. LFNIs are most typically used in ADDs on account of the improved water-sheeting action (especially from glass) which they confer to the ADD product. They also encompass non-silicone, nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

Preferred LFNIs include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/ polyoxypropylene reverse block polymers. The PO/EO/PO polymer-type surfactants are well-known to have foam suppressing or defoaming action, especially in relation to common food soil ingredients such as egg.

The invention encompasses preferred embodiments wherein LFNI is present, and wherein this component is solid at about 95°F (35°C), more preferably solid at about 77°F (25°C). For ease of manufacture, a preferred LFNI has a melting point between about 77°F (25°C) and about 140°F (60°C), more preferably between about 80°F(26.6°C) and 110°F (43.3°C).

In a preferred embodiment, the LFNI is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, excluding cyclic carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis.

A particularly preferred LFNI is derived from a straight chain fatty alcohol containing from about 16 to about 20 carbon atoms (C_{16}-C_{20} alcohol), preferably a C_{18} alcohol, condensed with an average of from about 6 to about 15 moles, preferably from about 7 to about 12 moles, and most preferably from about 7 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

The LFNI can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred LFNI surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Highly preferred ADDs herein wherein the LFNI is present make use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol fraction of the LFNI comprising from about 20% to about 80%, preferably from about 30% to about 70%, of the total LFNI.

Suitable block polyoxyethylene-polyoxypropylene polymeric compounds that meet the requirements described hereinbefore include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom, such as C_{12-18} aliphatic alcohols, do not generally provide satisfactory suds control in the instant ADDs. Certain of the block polymer surfactant compounds designated PLURONIC® and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention.

A particularly preferred LFNI contains from about 40% to about 70% of a polyoxypropylene/polyoxyethylene/polyoxypropylene block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and about 25%, by weight of the blend, of a block co-polymer of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane and containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylolpropane.

Suitable for use as LFNI in the ADD compositions are those LFNI having relatively low cloud points and high hydrophilic-lipophilic balance (HLB). Cloud points of 1% solutions in water are typically below about 32°C and preferably lower, e.g., 0°C, for optimum control of sudsing throughout a full range of water temperatures.

LFNIs which may also be used include a C_{18} alcohol polyethoxylate, having a degree of ethoxylation of about 8, commercially available SLF18 from Olin Corp. and any biodegradable LFNI having the melting point properties discussed hereinabove.

Anionic Co-surfactant

The automatic dishwashing detergent compositions herein can additionally contain an anionic co-surfactant. When present, the anionic co-surfactant is typically in an amount from 0 to about 10%, preferably from about 0.1% to about 8%, more preferably from about 0.5% to about 5%, by weight of the ADD composition.

Suitable anionic co-surfactants include branched or linear alkyl sulfates and sulfonates. These may contain from about 8 to about 20 carbon atoms. Other anionic cosurfactants include the alkyl benzene sulfonates containing from about 6 to about 13 carbon atoms in the alkyl group, and mono- and/or dialkyl phenyl oxide mono- and/or di-sulfonates wherein the alkyl groups contain from about 6 to about 16 carbon atoms. All of these anionic co-surfactants are used as stable salts, preferably sodium and/or potassium.

Preferred anionic co-surfactants include sulfobetaines, betaines, alkyl(polyethoxy)sulfates (AES) and alkyl (polyethoxy)carboxylates which are usually high sudsing. Optional anionic co-surfactants are further illustrated in published British Patent Application No. 2,116,199A; U.S. Pat. No. 4,005,027, Hartman; U.S. Pat. No. 4,116,851, Rupe et al; and U.S. Pat. No. 4,116,849, Leikhim, all of which are incorporated herein by reference.

Preferred alkyl(polyethoxy)sulfate surfactants comprise a primary alkyl ethoxy sulfate derived from the condensation product of a C_6-C_{18} alcohol with an average of from about 0.5 to about 20, preferably from about 0.5 to about 5, ethylene oxide groups. The C_6-C_{18} alcohol itself is preferable commercially available. C_{12}-C_{15} alkyl sulfate which has been ethoxylated with from about 1 to about 5 moles of ethylene oxide per molecule is preferred. Where the compositions of the invention are formulated to have a pH of between 6.5 to 9.3, preferably between 8.0 to 9, wherein the pH is defined herein to be the pH of a 1% solution of the composition measured at 20°C, surprisingly robust soil removal, particularly proteolytic soil removal, is obtained when C_{10}-C_{18} alkyl ethoxysulfate surfactant, with an average degree of ethoxylation of from 0.5 to 5 is incorporated into the composition in combination with a proteolytic enzyme, such as neutral or alkaline proteases at a level of active enzyme of from 0.005% to 2%. Preferred alkyl(polyethoxy)sulfate surfactants for inclusion in the present invention are the C_{12}-C_{15} alkyl ethoxysulfate surfactants with an average degree of ethoxylation of from 1 to 5, preferably 2 to 4, most preferably 3.

Conventional base-catalyzed ethoxylation processes to produce an average degree of ethoxylation of 12 result in a distribution of individual ethoxylates ranging from 1 to 15 ethoxy groups per mole of alcohol, so that the desired average can be obtained in a variety of ways. Blends can be made of material having different degrees of ethoxylation and/or different ethoxylate distributions arising from the specific ethoxylation techniques employed and subsequent processing steps such as distillation.

Alkyl(polyethoxy)carboxylates suitable for use herein include those with the formula $RO(CH_2CH_20)x CH_2C00\text{-}M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20%, preferably less than about 15%, most preferably less than about 10%, and the amount of material where x is greater than 7, is less than about 25%, preferably less than about 15%, most preferably less than about 10%, the average x is from about 2 to 4 when the average R is C_{13} or less, and the average x is from about 3 to 6 when the average R is greater than C_{13}, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl(polyethoxy)carboxylates are those where R is a C_{12} to C_{18} alkyl group.

Highly preferred anionic cosurfactants herein are sodium or potassium salt-forms for which the corresponding calcium salt form has a low Kraft temperature, e.g., 30°C or below, or, even better, 20°C or lower. Examples of such highly preferred anionic cosurfactants are the alkyl(polyethoxy)sulfates.

The preferred anionic co-surfactants of the invention in combination with the other components of the composition provide excellent cleaning and outstanding performance from the standpoints of residual spotting and filming. However, many of these co-surfactants may also be high sudsing thereby requiring the addition of LFNI, LFNI in combination with alternate suds suppressors as further disclosed hereinafter, or alternate suds suppressors without conventional LFNI components.

Amine Oxide

The ADD compositions of the present invention can optionally comprise amine oxide in accordance with the general formula I:

$$R^1(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2.qH_2O \qquad (I)$$

In general, it can be seen that the structure (I) provides one long-chain moiety $R^1(EO)_x(PO)_y(BO)_z$ and two short chain moieties, CH_2R'. R' is preferably selected represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Highly preferred amine oxides herein are solids at ambient temperature, more preferably they have melting-points in the range 30°C to 90°C. Amine oxides suitable for use herein are made commercially by a number of suppliers, including Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers. Preferred commercially available amine oxides are the solid, dihydrate ADMOX 16 and ADMOX 18 from Ethyl Corp.

Preferred embodiments include hexadecyldimethylamine oxide dihydrate, octadecyldimethylamine oxide dihydrate and hexadecyltris(ethyleneoxy)dimethylamine oxide.

Whereas in certain of the preferred embodiments R' = CH3, there is some latitude with respect to having R' slightly larger than H. Specifically, the invention further encompasses embodiments wherein R' = CH_2OH, such as hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide.

As noted, certain preferred embodiments of the instant ADD compositions comprise amine oxide dihydrates. Conventional processes can be used to control the water content and crystallize the amine oxide in solid dihydrate form. A new process comprises (a) conventionally making amine oxide as an aqueous solution or aqueous/organic solvent solution by reacting appropriate parent amine and aqueous hydrogen peroxide (for example, 50% H_2O_2); (b) drying the product to secure substantially anhydrous amine oxide (with or without an organic solvent being present to keep the viscosity low); (c) adding two mole equivalents of water per mole of amine oxide; and (d) recrystallizing the wet amine oxide from a suitable solvent, such as ethyl acetate.

In formulating the instant ADD compositions, the amine oxide may be added to an ADD composition as a powder. This is especially appropriate in the case of the amine oxide dihydrates, since these are nonhygroscopic solids. When it is desired to use the anhydrous form of the amine oxides, it is preferable to protect the amine oxide from moisture. It is contemplated to achieve this by conventional means, such as by applying a relatively nonhygroscopic coating, e.g., an anhydrous coating polymer, to amine oxide particles. Alternately, and more preferably, the anhydrous amine oxide should be melted with a conventional low-melting, low-foaming waxy nonionic surfactant which is other than an amine oxide material. Such surfactants are commonly used as "sheeting agents" in granular automatic dishwashing compositions and are illustrated more fully hereinafter (see description hereinbelow of low foaming nonionic surfactant or LFNI). A desirable process comprises heating the LFNI to just above its melting-point, then adding the amine oxide steadily to the heated LFNI, optionally (but preferably) stirring to achieve a homogeneous mixture; then, optionally (but preferably) chilling the mixture. When the LFNI has a lower melting point than the amine oxide, the amine oxide need not be completely melted at any stage. The above process illustrates a manner in which the time and extent of exposure of amine oxide to heat are minimized. Once co-melted into a suitable LFNI, the combined LFNI/amine oxide may be applied to an inorganic support, e.g., a pH-adjusting component described hereinafter). One suitable approach is to form an agglomerate comprising amine oxide, LFNI and water-soluble alkaline inorganic salt or water-soluble organic or inorganic builder. In another embodiment, the amine oxide in anhydrous form is melted with a solid-form alcohol or, preferably, an ethoxylated alcohol: this may be appropriate if more cleaning action is required and less sheeting action is desired (e.g., in geographies wherein rinse-aid use is common).

Preferred amine oxides herein are substantially free of amine and/or nitrosamine ("impurity"). Preferably, the amine oxide comprises less than about 2% free amine, more preferably about 1% or lower; and less than about 500 parts per billion, more preferably less than about 50 parts per billion by weight nitrosamine.

The present invention can contain from 0% to about 10%, preferably from about 1% to about 7%, more preferably from about 1.5% to about 1.5% of the long chain amine oxide; levels are generally expressed on an anhydrous basis unless otherwise specifically indicated.

Long-Chain Amine Oxide Solubilizing Aids

Although short-chain amine oxides do not provide the cleaning effect of the long-chain amine oxide component discussed above, short-chain amine oxides, such as octyldimethylamine oxide, decyldimethylamine oxide, dodecylamine oxide and tetradecylamine oxide may be added as solubilizing aids to the long-chain amine oxide. This is especially preferred if the composition is for use in cold-fill automatic dishwashing appliances. When present, a short-chain amine oxide solubilizer is preferably at not more than 1/10 of the total mass of the cleaning amine oxide component. Thus, levels of short-chain amine oxide are typically in the range from about 0 to about 2.0%, preferably about 0.1% to about 1% of the ADD composition. Moreover, it has been discovered that a short-chain amine oxide, if used, is preferably uniformly dispersed within the long-chain amine oxide rather than being added to the ADD in a separate particle.

When the granular automatic dishwashing compositions are destined for use in hot-fill automatic dishwashing appliances, e.g., those commonly available in the United States, the essential long-chain, amine oxide preferably comprises $R^1=C_{18}$ and is preferred over $R^1=C_{16}$ on grounds of mass efficiency; in this circumstance the use of short-chain amine oxide solubilizers is typically avoided.

Non-amine oxide solubilizing aids can be substituted, for example, solid-form alcohols or alcohol ethoxylates (the same as may be independently used for sheeting action or protection of the long-chain amine oxide from water discussed hereinabove).

Silicone and Phosphate Ester Suds Suppressors

The ADDs of the invention can optionally contain an alkyl phosphate ester suds suppressor, a silicone suds suppressor, or combinations thereof. Levels in general are from 0% to about 10%, preferably, from about 0.001% to about 5%. Typical levels tend to be low, e.g., from about 0.01% to about 3% when a silicone suds suppressor is used. Preferred non-phosphate compositions omit the phosphate ester component entirely.

Silicone suds suppressor technology and other defoaming agents useful herein are extensively documented in "Defoaming, Theory and Industrial Applications", Ed., P.R. Garrett, Marcel Dekker, N.Y., 1973, ISBN 0-8247-8770-6, incorporated herein by reference. See especially the chapters entitled "Foam control in Detergent Products" (Ferch et al) and "Surfactant Antifoams" (Blease et al). See also U.S. Patents 3,933,672 and 4,136,045. Highly preferred silicone suds suppressors are the compounded types known for use in laundry detergents such as heavy-duty granules, although types hitherto used only in heavy-duty liquid detergents may also be incorporated in the instant compositions. For example, polydimethylsiloxanes having trimethylsilyl or alternate endblocking units may be used as the silicone. These may be compounded with silica and/or with surface-active nonsilicon components, as illustrated by a suds suppressor comprising 12% silicone/ silica, 18% stearyl alcohol and 70% starch in granular form. A suitable commercial source of the silicone active compounds is Dow Corning Corp.

Levels of the suds suppressor depend to some extent on the sudsing tendency of the composition, for example, an ADD for use at 2000 ppm comprising 2% octadecyldimethylamine oxide may not require the presence of a suds suppressor. Indeed, it is an advantage of the present invention to select cleaning-effective amine oxides which are inherently much lower in foam-forming tendencies than the typical coco amine oxides. In contrast, formulations in which amine oxide is combined with a high-foaming anionic cosurfactant, e.g., alkyl ethoxy sulfate, benefit greatly from the presence of component (f).

Phosphate esters have also been asserted to provide some protection of silver and silver-plated utensil surfaces, however, the instant compositions can have excellent silvercare without a phosphate ester component. Without being limited by theory, it is believed that lower pH formulations, e.g., those having pH of 9.5 and below, plus the presence of the essential amine oxide, both contribute to improved silver care.

If it is desired nonetheless to use a phosphate ester, suitable compounds are disclosed in U.S. Patent 3,314,891, issued April 18, 1967, to Schmolka et al, incorporated herein by reference. Preferred alkyl phosphate esters contain from 16-20 carbon atoms. Highly preferred alkyl phosphate esters are monostearyl acid phosphate or monooleyl acid phosphate, or salts thereof, particularly alkali metal salts, or mixtures thereof.

It has been found preferable to avoid the use of simple calcium-precipitating soaps as antifoams in the present compositions as they tend to deposit on the dishware. Indeed, phosphate esters are not entirely free of such problems and the formulator will generally choose to minimize the content of potentially depositing antifoams in the instant compositions.

Detersive Enzymes (including enzyme adjuncts)

The compositions of this invention may optionally, but preferably, contain from 0 to about 8%, preferably from about 0.001% to about 5%, more preferably from about 0.003% to about 4%, most preferably from about 0.005% to about 3%, by weight, of active detersive enzyme. The knowledgeable formulator will appreciate that different enzymes should be selected depending on the pH range of the ADD composition. Thus, Savinase® may be preferred in the instant compositions when formulated to deliver wash pH of 10, whereas Alcalase® may be preferred when the ADDs deliver wash pH of, say, 8 to 9. Moreover, the formulator will generally select enzyme variants with enhanced bleach compatibility when formulating oxygen bleaches containing compositions of the present invention.

In general, the preferred detersive enzyme herein is selected from the group consisting of proteases, amylases, lipases and mixtures thereof. Most preferred are proteases or amylases or mixtures thereof.

The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or nonpurified forms of enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants. Particularly preferred by way of proteolytic enzyme is bacterial serine proteolytic enzyme obtained from Bacillus, Bacillus subtilis and/or Bacillus licheniformis. Suitable commercial proteolytic enzymes include Alcalase®, Esperase®, Durazym®, Savinase®, Maxatase®, Maxacal®, and Maxapem® 15 (protein engineered Maxacal); Purafect® and subtilisin BPN and BPN' are also commercially available. Preferred proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published

October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Most preferred is what is called herein "Protease C", which is a triple variant of an alkaline serine protease from Bacillus in which tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991, which is incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein. Some preferred proteolytic enzymes are selected from the group consisting of Savinase®, Esperase®, Maxacal®, Purafect®, BPN', Protease A and Protease B, and mixtures thereof. Bacterial serine protease enzymes obtained from Bacillus subtilis and/or Bacillus licheniformis are preferred. An especially preferred protease herein referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76 in combination with one or more amino acid residue position equivalent to those selected from the group consisting of +99, +101, +103, +107 and +123 in Bacillus amyloliquefaciens subtilisin as described in the concurrently filed patent application of A. Baeck, C.K. Ghosh, P.P. Greycar, R.R. Bott and L.J. Wilson, entitled "Protease-Containing Cleaning Compositions" and having U.S. Serial No.__________________ (P&G Case 5040). This application is incorporated herein by reference.

Preferred lipase-containing compositions comprise from about 0.001 to about 0.01% lipase, from about 2% to about 5% amine oxide and from about 1% to about 3% low foaming nonionic surfactant.

Suitable lipases for use herein include those of bacterial, animal, and fungal origin, including those from chemically or genetically modified mutants. Suitable bacterial lipases include those produced by Pseudomonas, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034, incorporated herein by reference. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase produced from the microorganism Pseudomonas fluorescens IAM 1057. This lipase and a method for its purification have been described in Japanese Patent Application 53-20487, laid open on February 24, 1978, which is incorporated herein by reference. This lipase is available under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Such lipases should show a positive immunological cross reaction with the Amano-P antibody, using the standard and well-known immunodiffusion procedure according to Oucheterlon (Acta. Med. Scan., 133, pages 76-79 (1950)). These lipases, and a method for their immunological cross-reaction with Amano-P, are also described in U.S. Patent 4,707,291, Thom et al., issued November 17, 1987, incorporated herein by reference. Typical examples thereof are the Amano-P lipase, the lipase ex Pseudomonas fragi FERM P 1339 (available under the trade name Amano-B), lipase ex Pseudomonas nitroreducens var. lipolyticum FERM P 1338 (available under the trade name Amano-CES), lipases ex Chromobacter viscosum var.lipolyticum NRRlb 3673, and further Chromobacter viscosum lipases, and lipases ex Pseudomonas gladioli. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272. Other lipases of interest are Amano AKG and Bacillis Sp lipase (e.g. Solvay enzymes). Additional lipases which are of interest where they are compatible with the composition are those described in EP A 0 339 681, published November 28, 1990, EP A 0 385 401, published September 5, 1990, EO A 0 218 272, published April 15, 1987, and PCT/DK 88/00177, published May 18, 1989, all incorporated herein by reference.

Suitable fungal lipases include those produced by Humicola lanuginosa and Thermomyces lanuginosus. Most preferred is lipase obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryzae as described in European Patent Application 0 258 068, incorporated herein by reference, commercially available under the trade name LipolaseR from Novo-Nordisk.

Any amylase suitable for use in a dishwashing detergent composition can be used in these compositions. Amylases include for example, a-amylases obtained from a special strain of B. licheniforms, described in more detail in British Patent Specification No. 1,296,839. Amylolytic enzymes include, for example, Rapidase™, Maxamyl™, Termamyl™ and BAN™. In a preferred embodiment, from about 0.001% to about 5%, preferably 0.005% to about 3%, by weight of active amylase can be used. Preferably from about 0.005% to about 3% by weight of active protease can be used. Preferably the amylase is Maxamyl™ and/or Termamyl™ and the protease is Savinase® and/or protease B. As in the case of proteases, the formulator will use ordinary skill in selecting amylases or lipases which exhibit good activity within the pH range of the ADD composition.

Enzyme Stabilizing System

Preferred enzyme-containing compositions, especially liquid 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.

The stabilizing system of the ADDs 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 dishwashing is usually large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are widely available, indeed ubiquitous, 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. In general, since the chlorine scavenger function can be performed by several of the ingredients separately listed under better recognized functions, (e.g., other components of the invention including oxygen bleaches), there is no requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any scavenger which is majorly incompatible with other optional ingredients, if used. For example, formulation chemists generally recognize that combinations of reducing agents such as thiosulfate with strong oxidizers such as percarbonate are not wisely made unless the reducing agent is protected from the oxidizing agent in the solid-form ADD composition. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in U.S. Patent 4,652,392, Baginski et al.

Dispersant Polymer

Preferred compositions herein may additionally contain a dispersant polymer. When present, a dispersant polymer in the instant ADD compositions is typically in the range from 0 to about 25%, preferably from about 0.5% to about 20%, more preferably from about 1% to about 7% by weight of the ADD composition. Dispersant polymers are useful for improved filming performance of the present ADD compositions, especially in higher pH embodiments, such as those in which wash pH exceeds about 9.5. Particularly preferred are polymers which inhibit the deposition of calcium carbonate or magnesium silicate on dishware.

Dispersant polymers suitable for use herein are illustrated by the film-forming polymers described in U.S. Pat. No. 4,379,080 (Murphy), issued Apr. 5, 1983, incorporated herein by reference.

Suitable polymers are preferably at least partially neutralized or alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanolammonium) salts of polycarboxylic acids. The alkali metal, especially sodium salts are most preferred. While the molecular weight of the polymer can vary over a wide range, it preferably is from about 1000 to about 500,000, more preferably is from about 1000 to about 250,000, and most preferably, especially if the ADD is for use in North American automatic dishwashing appliances, is from about 1000 to about 5,000.

Other suitable dispersant polymers include those disclosed in U.S. Patent No. 3,308,067 issued March 7, 1967, to Diehl, incorporated herein by reference. Unsaturated monomeric acids that can be polymerized to form suitable dispersant polymers include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence of monomeric segments containing no carboxylate radicals such as methyl vinyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 50% by weight of the dispersant polymer.

Copolymers of acrylamide and acrylate having a molecular weight of from about 3,000 to about 100,000, preferably from about 4,000 to about 20,000, and an acrylamide content of less than about 50%, preferably less than about 20%, by weight of the dispersant polymer can also be used. Most preferably, such dispersant polymer has a molecular weight of from about 4,000 to about 20,000 and an acrylamide content of from about 0% to about 15%, by weight of the polymer.

Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers. Such copolymers contain as monomer units: a) from about 90% to about 10%, preferably from about 80% to about 20% by weight acrylic acid or its salts and b) from about 10% to about 90%, preferably from about 20% to about 80% by weight of a substituted acrylic monomer or its salt and have the general formula:-$[(C(R^2)C(R^1)(C(O)OR^3]$- wherein the incomplete valencies inside the square braces are hydrogen and 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 and R^3 is sodium.

The low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of 3500 and is the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

Other suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents 4,530,766, and 5,084,535, both incorporated herein by reference.

Agglomerated forms of the present invention may employ aqueous solutions of polymer dispersants as liquid binders for making the agglomerate (particularly when the composition consists of a mixture of sodium citrate and sodium carbonate). Especially preferred are polyacrylates with an average molecular weight of from about 1,000 to about 10,000, and acrylate/maleate or acrylate/fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of unsaturated mono- and dicarboxylate monomers are disclosed in European Patent Application No. 66,915, published December 15, 1982, incorporated herein by reference.

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000 which can be obtained from the Dow Chemical Company of Midland, Michigan. Such compounds for example, having a melting point within the range of from about 30o to about 100oC can be obtained at molecular weights of 1450, 3400, 4500, 6000, 7400, 9500, and 20,000. Such compounds are formed by the polymerization of ethylene glycol or propylene glycol with the requisite number of moles of ethylene or propylene oxide to provide the desired molecular weight and melting point of the respective polyethylene glycol and polypropylene glycol. The polyethylene, polypropylene and mixed glycols are referred to using the formula $HO(CH_2CH_2O)_m(CH_2CH(CH_3)O)_n(CH(CH_3)CH_20)OH$ wherein m, n, and o are integers satisfying the molecular weight and temperature requirements given above.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Other suitable dispersant polymers are the carboxylated polysaccharides, particularly starches, celluloses and alginates, described in U.S. Pat. No. 3,723,322, Diehl, issued Mar. 27, 1973; the dextrin esters of polycarboxylic acids disclosed in U.S. Pat. No. 3,929,107, Thompson, issued Nov. 11, 1975; the hydroxyalkyl starch ethers, starch esters, oxidized starches, dextrins and starch hydrolysates described in U.S. Pat No. 3,803,285, Jensen, issued Apr. 9, 1974; the carboxylated starches described in U.S. Pat. No. 3,629,121, Eldib, issued Dec. 21, 1971; and the dextrin starches described in U.S. Pat. No. 4,141,841, McDanald, issued Feb. 27, 1979; all incorporated herein by reference. Preferred cellulose-derived dispersant polymers are the carboxymethyl celluloses.

Yet another group of acceptable dispersants are the organic dispersant polymers, such as polyaspartate.

Corrosion Inhibitor

The present compositions may also contain corrosion inhibitor. Such corrosion inhibitors are preferred components of machine dishwashing compositions in accord with the invention, and are preferably incorporated at a level of from 0.05% to 10%, preferably from 0.1% to 5% by weight of the total composition.

Suitable corrosion inhibitors include paraffin oil typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from 20 to 50: preferred paraffin oil selected from predominantly branched C_{25-45} species with a ratio of cyclic to noncyclic hydrocarbons of about 32:68; a paraffin oil meeting these characteristics is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

Other suitable corrosion inhibitor compounds include benzotriazole and any derivatives thereof, mercaptans and diols, especially mercaptans with 4 to 20 carbon atoms including lauryl mercaptan, thiophenol, thionapthol, thionalide and thioanthranol. Also suitable are the C_{12}-C_{20} fatty acids, or their salts, especially aluminum tristearate. The C_{12}-C_{20} hydroxy fatty acids, or their salts, are also suitable. Phosphonated octa-decane and other anti-oxidants such as betahydroxytoluene (BHT) are also suitable.

Other Optional Adjuncts

Depending on whether a greater or lesser degree of compactness is required, filler materials can also be present in the instant ADDs. These include sucrose, sucrose esters, sodium chloride, sodium sulfate, potassium chloride, potassium sulfate, etc., in amounts up to about 70%, preferably from 0% to about 40% of the ADD composition. Preferred filler is sodium sulfate, especially in good grades having at most low levels of trace impurities.

Sodium sulfate used herein preferably has a purity sufficient to ensure it is non-reactive with bleach; it may also be treated with low levels of sequestrants, such as phosphonates in magnesium-salt form. Note that preferences, in terms of purity sufficient to avoid decomposing bleach, applies also to component (b) ingredients.

Hydrotrope materials such as sodium benzene sulfonate, sodium toluene sulfonate, sodium cumene sulfonate, etc., can be present in minor amounts.

Bleach-stable perfumes (stable as to odor); and bleach-stable dyes (such as those disclosed in U.S. Patent 4,714,562, Roselle et al, issued December 22, 1987); can also be added to the present compositions in appropriate amounts. Other common detergent ingredients are not excluded.

Since certain ADD compositions herein can contain water-sensitive ingredients, e.g., in embodiments comprising anhydrous amine oxides or anhydrous citric acid, it is desirable to keep the free moisture content of the ADDs at a minimum, e.g., 7% or less, preferably 4% or less of the ADD; and to provide packaging which is substantially impermeable to water and carbon dioxide. Plastic bottles, including refillable or recyclable types, as well as conventional barrier cartons or boxes are generally suitable. When ingredients are not highly compatible, e.g., mixtures of silicates and citric acid, it may further be desirable to coat at least one such ingredient with a low-foaming nonionic surfactant for protection. There are numerous waxy materials which can readily be used to form suitable coated particles of any such otherwise incompatible components.

Method for Cleaning

The present invention also encompasses a method for cleaning soiled tableware comprising contacting said tableware with an aqueous medium having an initial range pH in a wash solution from about 8 to about 13, more preferably from about 9 to about 12, and comprising at least about 0.1% of a peroxygen bleach system, such as a peroxygen bleach and precursor, and a second coated pH adjusting component to yield a final wash pH between about 6.5 to about 9.5; preferably from about 7.0 to about 9.3 said aqueous medium being formed by dissolving a solid-form automatic dishwashing detergent containing in an automatic dishwashing machine. A particularly preferred method also includes low levels of silicate, preferably from about 0.5% to about 12% SiO_2.

The following examples illustrate the compositions of the present invention. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

EXAMPLE I

Granular automatic dishwashing detergents of the present invention are as follows:

Table 1

Ingredients	% by weight of active material A	B	C
Citrate	4.00	-	-
Coated citric acid[1]	15.00	26.80	21.50
Acusol 480N[2]	6.00	6.00	6.00
Sodium carbonate	9.00	---	---
Britesil H2O (as SiO_2)	8.50	--	--
Metasilicate (as SiO_2)	--	8.50	8.50

Alkyl ethoxy(3)sulfate	3.00	---	---
Nonionic surfactant[3]	---	3.00	3.00
Termamyl 60T	1.50	1.50	1.50
Protease D (4.6% prill)	1.60	---	---
Alcalase 2T	---	3.60	3.60
Percarbonate (Interox) (as AvO)	1.50	1.50	1.50
Benzoylvalerolactam	3.80	--	--
Benzoyloxybenzenesulphonate	--	3.80	--
Nonanoyloxybenzenesulphonate	--	--	3.80
Diethylene triamine penta methylene phosphonic acid	0.13	0.13	0.13
Polydimethylsiloxane	2.00	--	--
Sulfate, water, etc.	-------------------balance----------------		
Initial wash solution pH	10.2	12.00	12.00
Final wash solution pH	9.0	9.0	9.0

[1] Citric acid coated with 3.5% of paraffin wax/petrolatum/$C_{16}H_{33}(OC_2H_4)_{2.0}OH$ ratio of 96.5:2.5:1.

[2] From Rohm and Haas

[3] Low cloud point, high hydrophilic-lyphophilic balance

EXAMPLE II

Granular automatic dishwashing detergent containing silicate wherein glass care benefits are achieved are as follows:

Table 2

% by weight of active material

Ingredients	D	E	F
Citric acid	18.60	18.60	18.60
Acusol 480N[1]	6.00	6.00	6.00
Sodium carbonate	4.50	4.50	4.50
Britesil H2O (as SiO_2)	8.50	8.50	8.50
Alkyl ethoxy (3) sulfate	3.00	3.00	3.00
Termamyl 60T	1.50	1.50	1.50
Alcalase 2T	3.60	3.60	3.60
Percarbonate (Interox) (as AvO)	1.50	1.50	1.50
Benzoylvalerolactam	3.80	--	--
Benzoyloxybenzenesulphonate	-	3.80	--
Nonaroxybenzenesulphonate	--	--	3.80
Diethylene triamine penta methyl	--	--	--
phosphonic acid	0.13	0.13	0.13
Polydimethylsiloxane	2.00	2.00	2.00
Sulfate, water etc.	balance	balance	balance
pH	8.5	8.5	8.5

[1] Dispersant from Rohm and Haas

EXAMPLE III

Granular automatic dishwashing detergents containing silicate wherein glass care benefits are achieved are as follows:

Table 3

% by weight of active material

Ingredients	G	H	I
Citrate	1.25	10.00	10.00
Citric acid	17.50	11.00	11.00
Acusol 480N[1]	6.00	6.00	--
Polyaspartate	--	--	6.00
Sodium carbonate	15.50	--	--
Sodium bicarbonate	--	20.00	20.00

Britesil H2O(as SiO_2)	8.50	8.50	8.50
Nonionic surfactant[2]	2.00	3.00	3.00
Termamyl 60T	1.50	1.50	1.50
Alcalase 2T	3.60	3.60	3.60
Perborate monohydrate (as AvO)	1.50	1.50	1.50
Benzoyloxybenzenesulphonate	3.80	--	--
Benzoylcaprolactam	--	3.80	--
Nonaoxybenzenesulphonate	--	--	3.80
Diethylene triamine penta acetic acid	0.13	0.13	0.13
Sulfate, water, etc.	---------------balance---------------------		
pH	9.0	9.0	9.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

EXAMPLE IV

Granular automatic dishwashing detergents containing silicate wherein glass care benefits are achieved are as follows:

Table 4

% by weight of active material

Ingredients	J	K	L
Citrate	15.00	15.00	20.00
Acusol 480N[1]	6.00	6.00	6.90
Sodium carbonate	20.00	20.00	23.00
Britesil H2O (SiO_2)	9.00	9.00	7.50
Nonionic surfactant[2]	2.00	2.00	2.00
Savinase 12T	2.00	2.00	2.00
Termamyl 60T	1.00	1.00	1.00
Percarbonate (as AvO)	1.50	1.50	1.50
Benzoylcaprolactam	2.00	3.80	2.00
Diethylene triamine penta acetic acid	0.13	0.13	0.13
1,1-hydroxyethane diphosphonic acid	0.50	0.50	0.50
Sulfate, water, etc.	---------------balance---------------------		
pH	10.0	10.0	10.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

Table 5

% by weight of active material

Ingredients	M	N	O
Citrate	20.00	20.00	20.00
Acusol 480N[1]	6.90	6.90	6.90
Sodium carbonate	23.00	23.00	23.00
Britesil H2O (as SiO_2)	7.50	7.50	7.50
Nonionic surfactant[2]	2.00	2.00	2.00
Savinase 12T	2.00	2.00	2.00
Termamyl 60T	1.00	1.00	1.00
Percarbonate (as AvO)	1.00	1.50	1.50
Benzoylcaprolactam	2.00	3.80	3.80
Diethylene triamine penta acetic acid	0.13	0.13	--
S,S-Ethylene diamine disuccinate	--	--	0.13
1,1-hydroxyethane diphosphonic acid	0.50	0.50	0.50
Sulfate, water, etc.	----------------balance----------------------		
pH	10.0	10.0	10.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

Table 6

% by weight of active material

Ingredients	P	Q	R
Citrate	20.00	20.00	20.00
Acusol 480N[1]	6.90	6.90	6.90
Sodium carbonate	23.00	23.00	23.00
Britesil H_2O (as SiO_2)	7.50	7.50	7.50
Nonionic surfactant[2]	2.00	2.00	2.00
Savinase 12T	2.00	2.00	2.00
Termamyl 60T	1.00	1.00	1.00
Percarbonate (as AvO)	1.50	1.00	1.50
Benzoylvalerolactam	3.80	2.00	--
Benzoylxybenzenesulphonate	--	--	3.80
S,S-ethylene diamine disuccinate	0.13	0.13	0.13
1,1-hydroxyethane diphosphonic acid	0.50	0.50	0.50
Sulfate, water, etc.	----------------balance----------------------		
pH	10.0	10.0	10.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

Table 7

% by weight of active material

Ingredients	S	T	U
Citrate	15.00	20.00	20.00
Acusol 480N[1]	6.00	6.90	6.90
Sodium carbonate	20.00	23.00	23.00
Britesil H2O (as SiO_2)	9.00	7.50	7.50
Nonionic surfactant[2]	2.00	2.00	2.00
Savinase 12T	2.00	2.00	2.00
Termamyl 60T	1.00	1.00	1.00
Perborate monohydrate (as AvO)	1.50	1.50	--
Percarbonate (as AvO)	--	--	1.50
C_8 - OBS	--	--	1.20
C_9 - OBS	2.00	2.00	--
C_{10} - OBS	--	--	0.80
Diethylene triamine penta acetic acid	0.13	0.13	--
S,S-ethylene diamine disuccinate	--	--	0.13
Sulfate, water, etc.	----------------balance----------------------		
pH	10.0	10.0	10.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

Table 8

% by weight of active material

Ingredients	V	W	X
Citrate	20.00	20.00	20.00
Acusol 480N[1]	6.90	6.90	6.90
Sodium carbonate	23.00	23.00	23.00
Britesil H2O (as SiO_2)	7.50	7.50	7.50
Nonionic surfactant[2]	2.00	2.00	2.00
Savinase 12T	2.00	2.00	2.00
Termamyl 60T	1.00	1.00	1.00
Percarbonate (as AvO)	1.00	1.50	0.75
C_8 - OBS	1.20	2.30	2.30
C_{10} - OBS	0.80	1.50	1.50
S,S-ethylene diamine disuccinate	0.13	0.13	0.13
Sulfate, water, etc.	----------------balance----------------------		

pH	10.0	10.0	10.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

Table 9

	% by weight of active material
Ingredients	Y
Citrate	20.00
Acusol 480N[1]	6.90
Sodium carbonate	23.00
Britesil H2O (as SiO_2)	7.50
Nonionic surfactant[2]	2.00
Savinase 12T	2.00
Termamyl 60T	1.00
Percarbonate (as AvO)	0.75
C_8 - OBS	3.00
C_{10} - OBS	2.00
SS-EDDS	0.13
Sulfate, water, etc.balance	
pH	10.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

Table 10

	% by weight of active material		
Ingredients	Z	AA	BB
Citrate	29.00	29.00	29.00
Acusol 480N[1]	6.00	6.00	6.00
Sodium carbonate			
Britesil H_2O (as SiO_2)	17.00	17.00	17.00
1,1-hydroxyethane diphosphonic acid	0.50	0.50	0.50
Nonionic surfactant[2]	1.50	1.50	1.50
Savinase 12T	2.00	2.20	2.20
Termamyl 60T	1.50	1.50	1.50
Perborate monohydrate (as AvO)	0.30	0.30	0.30
Perborate tetrahydrate (as AvO)	0.90	0.90	0.90
Benzoylcaprolactam	3.80	7.00	--
Benzoylvalerolactam	--	--	7.00
Diethylene tiramine penta			

methylene	0.50	0.50	0.05
phosphonic acid	0.13	0.13	0.13
Paraffin	0.50	0.50	0.50
Benzotriazole	0.30	0.30	0.30
Sulfate, water, etc.	----------------balance----------------------		
pH	10.0	10.0	10.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

Table 11

% by weight of active material

Ingredients	CC	DD
Citrate	29.00	29.00
Acusol 480N[1]	6.00	6.00
Sodium carbonate	5.00	5.00
Sodium Metasilicate	9.80	9.80
1,1-hydroxyethane diphosphonica acid	0.50	0.50
Nonionic surfactant[2]	1.50	1.50
Savinase 12T	2.00	2.20
Termamyl 60T	1.50	1.50
Percarbonate (as AvO)	1.20	1.20
Benzoylvalerolactam	--	3.80
Benzoylcaprolactam	3.80	--
Diethylene triamine penta methyl phosphonic acid	0.13	0.13
Paraffin	0.50	0.50
Benzotriazole	0.30	0.30
Sulfate, water, etc.	----------------balance----------------------	
pH	10.0	10.0

[1] Dispersant from Rohm and Haas

[2] Low cloud, high HLB nonionic surfactant

EXAMPLE V

Table 11

Builder	EE	FF
Sodium citrate dihydrate	33.0	
Sodium tripolyphosphate	-	46.0
Sodium metasilicate	9.9	9.9
Sodium carbonate	10.1	10.1)
1,1-hydroxyethane diphosphonic acid	0.83	0.83
PA30	4.0	4.0
Perborate monohydrate (asAvO)	1.95	1.95
Perborate tetrahydrate (as AvO)	8.65	8.65
Benzoyloxybenzene sulfonate	4.78	4.78
Diethylene triamine penta methyl phosphonic acid	0.65	0.65
Savinase 12T/Termamyl 60T	3.7	3.7
Betahydroxytoluene	0.3	0.3
Paraffin	0.5	0.5
Nonionic[1]	1.5	1.5
Sodium Sulphate, minors	------------ balance ------------	

[1] Plurafac LF404

EXAMPLE VI

Tablet compositions of the present invention are as follows:

Table 12

Builder	GG	HH	II	JJ
Citrate	20.9	20.9	16.7	--
Phosphate	--	--	--	25.8
Acrylic acid/Maleic acid co-polymer	--	--	11.1	--
PA30	2.7	2.7	--	--
Carbonate	14.0	14.0	--	1.6
Bicarbonate	--	--	48.6	--
1,1-hydroxyethane diphosphonic acid	0.36	0.36	--	--
Silicate 2r(SiO_2)	12.2	12.2	--	--
metaSilicate (SiO_2)	--	--	--	44.8
Paraffin	0.36	0.36	0.2	0.2
Benzotriazole	0.21	0.21	--	--
Perborate tetrahydrate (as AvO)	0.64	0.64	0.64	--
Perborate monohydrate ...(as AvO)	0.22	0.22	--	--
Percarbonate (as AvO)	--	--	--	1.00
Benzoylcaprolactam	3.2	5.1	5.0	--
Phenylbenzoate	--	--	--	5.00
Diethylene triamine penta methylene phosphoric acid	0.09	0.09	--	--
Savinase 6T	--	--	1.15	--
Savinase 12T	1.58	1.58	--	--
Termamyl 60T	1.1	1.1	1.0	--
Nonionic surfactant	1.18	1.18	0.8	--
Sulphate, water, minors	-------------------- balance --------------------			
pH	11.0	11.0	9.5	12.6

EXAMPLE VII

Granular automatic dishwashing detergents containing manganese complexes wherein stain removal benefits are achieved ar as follows:

Ingredients	KK	LL
Mn Catalyst[3]	Same as K however add 300 ppm and reduce 3.80 to 1.9	Same as P however add 300 ppm and reduce 3.8 to 1.9

[3] 1:1 mole ratio of Mn cation and liquand to form Mn^{1V}_2 $(u\text{-}0)_3$(1,4,7-trimethyl-1,4,7-triacyclononane)$_2$-$(PF_6)_2$ in site or performed.

Claims

1. An automatic dishwashing detergent composition comprising:
   (a) from 0.01% to 8%, available oxygen (AvO) added as a peroxygen bleach selected from the group consisting of percarbonate, perborate, monopersulfate and mixtures thereof;
   (b) from 0.01% to 10%,of bleach activator selected from the group consisting of benzoyloxybenzenesulphonate, benzoylcaprolactam, benzoylvalerolactam, nonanoyloxybenzenesulphonate, phenylbenzoate derivatives; and mixtures thereof; and
   (c) from 0.1% to 50%, of pH adjusting component, said component providing a wash solution pH from 8 to 13;
   wherein said composition comprises a molar ratio of AvO to bleach activator of at least 1:1 characterized in enhanced stain removal.

2. A composition according to Claim 1 wherein said peroxygen bleach activator is selected from the group consisting of benzoylcaprolactam, 4-nitrobenzoylcaprolactam, 3-chlorbenzoylcaprolactam, nonanoyloxybenzenesulphonate, heptaoyloxybenzenesulphonate, benzoylvalerolactam, octanoyloxybenzenesulphonate, and mixtures thereof.

3. A composition according to Claim 1 or 2 further comprising from 0.1% to 10% of a low foaming nonionic surfactant selected from the group consisting of alkoxylated alcohols, glucosamides and mixtures thereof.

4. A composition according to any one of the preceding claims wherein said wash solution pH is from 9.0 to 12.0 and wherein said pH adjusting component of (c) is a salt or salt/builder mixture selected from
   (i) sodium carbonate or sesquicarbonate
   (ii) sodium citrate
   (iii) citric acid
   (iv) sodium bicarbonate
   (v) sodium borate
   (vi) sodium hydroxide; and
   (vii) mixtures thereof.

5. A composition according to any one of the preceding claims further comprising from 0.001% to 5% of a detersive enzyme selected from the group consisting of protease, amylase, lipase, from 0.005 to 3% by weight protease or amylase, and mixtures thereof.

6. A composition according to any one of the preceding claims comprising from 0.5% to 3% available oxygen and wherein said ratio of AvO to bleach activator is from 20:1 to 1:1.

7. A composition according to any one of the preceding claims wherein said peroxygen bleach compound is selected from the group consisting of percarbonate salts or perborate salts and wherein said peroxygen bleach activator is 3-chlorobenzoylcaprolactam or benzoylvalerolactam.

8. A composition according to any one of the preceding claims further comprising bleach catalyst is selected from the group consisting of Mn$^{IV}_2$(u-O)$_3$(1,4,7-trimethyl-1,4,7-triacyclononane)$_2$-(PF$_6$)$_2$, Mn$^{III}_2$(u-O)$_1$(u-OAc)$_2$(1,4,7-tri-methyl-1,4,7-triacyclononane)$_2$-(ClO$_4$)$_2$; Mn$^{IV}_4$(u-O)$_6$(1,4,7-triacyclononane)$_4$-(ClO$_4$)$_2$; Mn^{III}Mn$^{IV}_4$(u-O)$_1$(u-OAc)$_2$ (1,4,7-tri-methyl-1,4,7-triacyclononane)$_2$-(ClO$_4$)$_3$; Mn(1,4,7-trimethyl-1,4,7-triazacyclononane(OCH$_3$)$_3$(PF$_6$); Co(2,2'-bispyridyl-amine)Cl$_2$; Di-(isothiocyanato)bispyridylamine-cobalt (II); trisdipyridylamine-cobalt (II) perchlorate; Co(2,2-bispyridylamine)$_2$- O$_2$ClO$_4$; Bis-(2,2'-bispyridylamine) copper(II) per-chlorate; tris(di-2-pyridylamine) iron (II) perchlorate; Mn gluconate; Mn(CF$_3$SO$_3$)$_2$; Co(NH$_3$)$_5$Cl; binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including N$_4$Mn^{III}(u-O)$_2$Mn^{IV}N$_4$)$^+$and [Bipy$_2$Mn^{III}(u-O)$_2$Mn^{IV}bipy$_2$]-(ClO$_4$)$_3$ and mixtures thereof.

9. A granular composition according to any one of the preceding claims further comprising from 0.5% to 12% SiO$_2$.

10. A composition according to any one of the preceding claims further comprising from 0.5% to 20% of a dispersant polymer selected from the group consisting of polyacrylates and polyacrylate copolymers..

11. A liquid composition according to any one of the preceding claims further comprising from 0.01% to 6% by weight of an enzyme stabilizing system.

12. A granular or powdered automatic dishwashing detergent composition which comprises by weight:

(a) from 0.3% to 4% of available oxygen added as a peroxygen bleach component selected from the group consisting of percarbonate, perborate and mixtures thereof;
(b) from 0.8% to 5% bleach activator selected from the group consisting of benzoylcaprolactam, benzoylvaerolactam, benyoyloxybenzenesulphonate, and mixtures thereof;
(c) from 0.1% to 50% of a pH adjusting component consisting of water-soluble salt or salt/builder mixture selected from sodium carbonate, sodium sesquicarbonate, sodium citrate, citric acid, sodium bicarbonate, sodium hydroxide, and mixtures thereof;
(d) from 1% to 11% silicate;
(e) from 0 to 10% of a low-foaming nonionic surfactant other than amine foxide;
(g) from 0 to 10% of an anionic cosurfactant;
(h) from 0 to 2% of a short-chain amine oxide; (i) from 0 to 10% of a silicone suds suppressor;
(j) from 0.001% to 5% of an active detersive enzyme;
(k) from 0 to 25% of a dispersant polymer; and
(l) from 0 to 40% of sodium sulfate,

wherein said composition has a molar ratio of AvO to peroxygen bleaching compound of from 20:1 to 1:1 and a wash solution pH from 9.5 to N.

13. A method for cleaning soiled tableware comprising contacting said tableware with a pH wash aqueous medium of at least 8 and comprising at least 0.1% available oxygen added as peroxygen bleach and at least 0.01% of bleach activator selected from the group consisting of benzoylvalerolactam or benzoylcaprolactam.