

(19)



Europäisches Patentamt

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Office européen des brevets



(11)

EP 0 723 006 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.07.1996 Bulletin 1996/30

(51) Int. Cl.⁶: **C11D 3/39**, C11D 3/386

(21) Application number: **95203545.9**

(22) Date of filing: **19.12.1995**

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT SE

- **Showell, Michael S.**
Cincinnati, Ohio 45224 (US)
- **Burckett-St. Laurent, James C. T. R.**
Cincinnati, Ohio 45249 (US)

(30) Priority: **23.01.1995 US 376604**

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

(74) Representative: **Pike, Christopher Gerard et al**
Procter & Gamble Limited,
Whitley Road,
Longbenton
Newcastle upon Tyne NE12 9TS (GB)

(72) Inventors:
• **Surutzidis, Athanasios**
Hamilton, Ohio 45011 (US)

(54) **Cleaning methods and products providing compatibilized staged release of bleach followed by enzymes**

(57) Improved detergent compositions, especially granular automatic dishwashing detergents, comprising detergent enzymes (such as proteases and/or amylases), and bleaches (such as hypochlorite or sodium dichloroisocyanurate) capable of deactivating the enzymes. Also, methods for achieving improved performance from combinations of these ingredients via an improved delivery sequence and profile, specifically involving release of bleach prior to enzyme, are provided. Preferred compositions comprise bleach scavengers (such as ammonium sulfate) and enzyme dissolution-delaying polymers (such as film-forming polyesters) employed in compositions which allow destruction of the bleach or its conversion to an enzyme-compatible form prior to dispersal of enzyme in the wash.

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DescriptionFIELD OF THE INVENTION

5 This invention relates to detergent compositions, especially enzyme/bleach-containing detergent compositions, and to methods for machine dishwashing in a domestic dishwasher.

BACKGROUND OF THE INVENTION

10 Automatic Dishwashing is a demanding field in which specialized detergent formulations are required to deliver efficient and effective sanitization and cleansing of dishware, including stain removal and tough food cleaning. Automatic Dishwashing has some unique constraints as compared to fabric laundering, for example, spotlessness and lack of film is desired on glasses and silverware. In many laundering operations, in contrast, there is a tolerance for substances which may be greasy, oily, soapy or lubricious, often fabric softeners or fatty acid salts, being deposited on fabrics.

15 In modern automatic dishwashing formulations, tough food cleaning performance is essential, and this is commonly accomplished by deterative enzymes. Alkalis are also used, but may be highly corrosive, especially at high levels. Stain removal is best accomplished by a variety of bleaches.

Owing to the enzyme-deactivating nature of some of the most effective bleaches, especially hypochlorite bleaches, compromise detergent formulations have often been provided. This includes formulations in which a relatively mild and enzyme-compatible bleach, such as perborate, is combined with the enzymes; optionally with activators. Such formulations are commercially available in some geographies.

20 Various efforts have been made to increase the compatibility of deterative enzymes with deactivating materials. Such efforts include the engineering of improved enzymes and the provision of stabilized enzyme particles for fabric laundering. The latter can contain one or more stabilizing agents, anti-oxidants, or bleach scavengers. The types and amounts of such agents are selected to enhance product stability on storage or to improve enzyme stability when a domestic water supply contains, as it commonly does for health reasons, a certain limited amount of free chlorine.

25 Thus U.S. Patents 3,755,085, Tivin, issued Sept. 30, 1970 and 3,893,954, Tivin, issued July 8, 1975, describe detergent compositions for fabric laundering containing enzyme and chlorine scavenger such as tris(hydroxymethyl)aminomethane and a variety of additional amino alcohols. U.S. Patent 4,810,413, Pancheri et al, issued Mar. 7, 1989, describes granular detergent compositions, exemplified by fabric laundering detergents, comprising an enzyme component that is inactivated by free chlorine, a chlorine scavenger which is a salt containing an ammonium cation, a detergent surfactant, and a detergent builder. Chlorine scavengers described include not only ammonium salts but anions such as sulfite, bisulfite, thiosulfite, thiosulfate, carbamate and ascorbate, and combinations thereof.

30 Machine Dishwashing by use of tablets for the sequential release of different materials, which can include bleach and enzymes, is described in EP 481, 547 A1, published April 22, 1994, by Unilever NV. It is taught that delaying the release of bleach provides superior results. This system is a macro-particle having, on one hand convenience, but on the other hand, the known disadvantages of tablets as compared to granular detergents.

35 U.S. Patent 5,324,649, Arnold et al, issued Jun. 28, 1994, describes enzyme-containing granules coated with hydrolyzed polyvinyl alcohol or copolymer thereof, optionally further comprising a chlorine scavenger and/or other materials such as a lubricant. These particles very rapidly release their enzyme activity, as shown, for example, by Fig. 3 of this patent in which enzyme activity released from the granule reaches a maximum after only about one minute. Usefully for purposes of background herein, Arnold et al describe common enzyme-processing and coating operations, pigments or process additives such as Titanium Dioxide useful for producing acceptably colored enzyme particles, substances which can be present in commercial enzyme broths, enzyme cores and core materials, and enzyme protecting agents or scavengers such as ammonium sulfate, ammonium citrate, urea, guanidine hydrochloride, guanidine carbonate, guanidine sulfonate, thiourea dioxide, monoethanolamine, diethanolamine, triethanolamine, amino acids such as glycine, sodium glutamate and the like, and proteins such as bovine serum albumin, casein and the like.

40 U.S. Patent 4,973,417, Falholt, issued Nov. 27, 1990, describes enteric coated detergent enzymes, optionally comprising anti-oxidants. It is explained therein that this improves stability of the enzyme granules in humid environments in presence of strongly oxidizing bleaches. Other aspects of the disclosure useful for background purposes herein include description of "cores" exhibiting particle sizes between 2 and 2000 micron, fluid bed processing such as Wurster bed processing or rotor bed (Glatt) processing, and specific copolymers such as copolymers of methacrylic acid and an acrylic acid ester, preferably a methyl or ethyl ester, which are used to produce the coating. Such polymers have low solubility at pH = 6 but have solubility which rises rapidly for pH values above 6. Fillers, plasticizers and the like may be used to produce the enteric coated enzyme particles and antioxidant such as sodium bisulfite or ascorbate may be used.

45 U.S. Patent 5,254,283, Arnold and Becker, issued Oct. 19, 1993, describes isophthalic polymer-coated particles which comprise enzymes and oxidant scavengers or enzyme protecting agents. Fig. 1 of this patent shows a rapid

release of ammonium sulfate starting at time = 0 and reaching a maximum at 0.5 minutes, and a gradually increasing release of enzyme starting also at time = 0 and reaching a maximum at about 2 minutes.

Other approaches to compatibilize enzymes with bleaches for increased storage stability or treatment of chlorine in the water supply include coating the bleach component, using clay coatings on enzyme and/or on bleach, and the like.

Regardless of the efforts made especially in storage stabilization and avoidance of enzyme "shock" from chlorinated water, and even in the area of sequencing the delivery of ingredients in tablets, no completely satisfactory solutions have been found leading to the successful commercial introduction of automatic dishwashing granules comprising effective amounts of enzyme-deactivating bleach and detergent enzymes such as proteases and amylases in a compatible fashion. Moreover, enzyme particles now typically available for use in automatic dishwashing have one or more shortcomings in the areas of bleach compatibility, spotting/filming, storage stability and the like.

Since hypochlorite and similar enzyme-deactivating bleaches are highly reactive, it would have been expected that the best way to sequentially deliver such bleaches with enzymes in automatic dishwashing would be to release the enzyme first, permit it to work for an extended period to best effect, and then "finish" the cleaning operation with a short burst of the quickly-acting enzyme-deactivating bleach. In terms of detergent design this suggests (a) coating the bleach and (b) maximizing the rapid release of enzymes after adventitious chlorine in the wash water has been scavenged. Such logic would lead the formulator of automatic dishwashing granules to select, from the range of release profiles of commercial enzymes, those enzymes which are fast-released, after an initial delivery of some scavenger to treat the water. Bleach coatings are known. See U.S. Patent 4,867,895, Choy, issued Sept. 19, 1989, and the hereinbefore referenced EP 481,574 A.

Despite the above putative sequence, it has now unexpectedly been discovered that for automatic dishwashing purposes, excellent bleaching and enzymatic action are obtained in a staged release operation in which first, a rapidly-acting bleach is delivered and allowed to act for a limited period, for example a few minutes; then this bleach, along with any chlorine which may originally have been in the water, are destroyed or converted to an enzyme-compatible form (in either case "compatibilized" with detergent enzyme) using an effective, preferably "more-than-chlorine-scavenging" amount of a bleach scavenger (the phrase "more than scavenging" referring to the fact that significantly more scavenger is needed than the amount which would be needed merely to deal with the chlorination of the water supply); and then, for a third, and now more substantial time period, the enzyme component of the granular automatic dishwashing detergent formulation is provided and allowed to act.

This discovery leads to a specific selection in an automatic dishwashing detergent of those enzyme particles which delay release of enzyme to a greater extent than is considered ideal for laundry or chlorinated water control purposes, yet to a lesser extent than would be observed from the use of say, a typical agricultural fertilizer coating and its associated release profile.

Without intending to be limited by theory, it is believed that the early release of the enzyme-deactivating bleach coincides with a time period in the overall wash operation in which food soils have been dispersed to the minimum extent. This minimizes wasteful reaction of the bleach with dispersed food soil and permits it to react to good effect with colored stains or deposits on the dishware. Later in the wash, food soils, often "dried-on" food, are dispersed, and as is known, actually assist in stabilizing the later-released enzymes as they perform their more leisurely, but nonetheless vital action.

It is therefore an object herein to provide an improved granular detergent comprising detergent enzymes, bleach scavengers, enzyme-deactivating bleaches and certain coating polymers, in a format engineered to deliver staged release of the desired ingredients, especially in the washing process of commercial domestic automatic dishwashing appliances, so that the sum of stain-removing, cleaning and spotting/filming benefits of the bleach and enzymes is maximized. Other objects include the provision of improved methods for providing compatibilized staged release of bleaches followed by enzymes in a cleaning operation.

BACKGROUND ART

Controlled Release Technology (Agricultural, Pharmaceutical), Coating Processes (Powder Technology, Spray Technology), Bleaching Agents, Enzymes, and Ammonium Salts are reviewed in Kirk Othmer, Encyclopedia of Chemical Technology, Fourth Edition, John Wiley and Sons, New York, incorporated by reference. See also the hereinbefore referenced U.S. 3,755,085, 3,893,954, 4,810,413, 5,324,649, 4,973,417 and 5,254,283; as well as EP 481,547 A.

SUMMARY OF THE INVENTION

The present invention relates to a detergent composition for the release of bleach followed by enzyme, said composition comprising: (a) at least one enzyme-deactivating bleach, such as a hypochlorite, for example in the form of sodium dichloroisocyanurate; (b) at least one bleach scavenger, for example ammonium sulfate or sodium bisulfite; and (c) at least one detergent enzyme, for example a mixture of protease and amylase; and wherein further, upon mixing

with water, said detergent composition begins releasing: (i) a stain-removal effective amount of said enzyme-deactivating bleach, followed by (ii) a compatibilizing amount of said bleach scavenger, followed thereafter by (iii) a cleaning-effective amount of said detergent enzyme.

5 Critical herein is the notion of "compatibilizing" the enzyme with the bleach. The term "compatibilizing" for the present purposes encompasses (1) irreversibly reacting the bleach to destroy it, for example using sodium bisulfite or a hydrogen peroxide source as bleach scavenger; or (2) chemically reacting the bleach to convert it to an enzyme-compatible form, for example by forming an N-halo compound which releases hypochlorite with difficulty or (3) suppressing the dissociation of an N-halo compound which readily releases hypochlorite, by means of a hydrolysis-suppressing amount of bleach scavenger. Accordingly, in general, a "compatibilizing amount" of bleach scavenger may vary quite
10 widely depending upon the precise bleach scavenger selected. Nonetheless, it will be clear that a "compatibilizing amount" of bleach scavenger is generally substantially in excess of the amount required either to measurably improve storage stability of enzymes, or to deal with the typical low levels of chlorine in chlorinated water supplies.

The terms "stain removal effective amount" and "cleaning-effective amount" encompass typical levels of the ingredients referred to as used in automatic dishwashing, and, along with "compatibilizing" amounts, are further illustrated in
15 detail hereinafter.

In preferred embodiments of the instant detergent compositions, there is moreover a requirement that a specific dissolution profile of the detergent be respected. A "dissolution profile" herein refers to the release with time into a washing solution of the detergent ingredients, especially the aforementioned enzyme-deactivating bleach, bleach scavenger and enzyme. "Dissolution" need not proceed to the molecular level, provided that ingredients become available
20 for cleaning action, chemical reaction with each other, or other practical measures. Accordingly, in a preferred embodiment, the invention encompasses a detergent composition for use in a washing appliance, said detergent composition having granular form and further, having a dissolution profile releasing substantially all of said stain-removal effective amount of said enzyme-deactivating bleach in no more than about the first 75%, more preferably in no more than about 50%, more preferably still, no more than a period less than 50% of a wash cycle of said appliance. The term "substantially all" is intended to refer to the maximum amount practically deliverable, which is typically somewhat less than
25 100%, resulting from minor amounts of clumping or loss on the walls of the appliance. With reference to a dissolution profile which is graphically represented as amount of ingredient released vs time, said percentages are simply percentages of the total time a wash cycle of the appliance requires. Appliances can vary in "wash cycle" or "cycle time", typically depending on the geography in which they are prevalent.

The present invention further provides improved granular automatic dishwashing detergents and improved cleaning methods, which may either rely on said granular detergent or may be independent of any particular product form. More preferably, detergent compositions herein have the form of granular automatic dishwashing detergents for use in domestic automatic dishwashing appliances wherein further, the detergent composition has a dissolution profile releasing more than 50% of said cleaning-effective amount of said detergent enzyme no sooner than about 2 minutes into a
30 wash cycle of said appliance. More preferably still, said dissolution profile is one releasing more than 50% of said compatibilizing amount of said bleach scavenger no sooner than about 1 minute into a wash cycle of said appliance. Accordingly, it will be understood and appreciated that the preferred detergent compositions herein differ particularly in the total amounts of ingredients delivered, and in their dissolution with time, as compared to conventional detergents.

The present invention also encompasses a detergent composition comprising: (a) a plurality of particles of a first
40 kind, each comprising: (i) one or more detergent enzymes, (ii) one or more bleach scavengers, surrounding or admixed with said detergent enzymes, and (iii) one or more coating layers comprising a coating polymer and at least partially separating said detergent enzymes from at least a portion of said bleach scavengers; and (b) a plurality of particles of a second kind, each comprising at least one enzyme-deactivating bleach; whereby, when said detergent composition is dispensed into water in an automatic dishwashing appliance, the concentration of said enzyme-deactivating bleach
45 is reduced to less than about 1 ppm prior to the release of no more than about 50% of said detergent enzyme, on a weight basis. Thus, coating polymers, as are more fully described and illustrated hereinafter, are used as one manner of practically delivering the desired dissolution profiles.

The present invention also provides a method for compatible (or compatibilized - these terms having the same connotations as introduced in connection with "compatibilizing", supra) staged release of an enzyme-deactivating bleach
50 followed by one or more detergent enzymes in an aqueous washing process in a domestic washing appliance [preferably a domestic automatic dishwashing appliance having the customary high-shear water spraying action (which differs from the action of conventional fabric laundering appliances)] having at least one wash cycle of finite total duration (such duration can differ quite widely, for example some wash cycles are only about 5 minutes in duration whereas others can extend for an hour or longer). Said method comprises (a) a step of releasing, in a first period starting at about
55 30 sec. into said cycle and finishing at a time which is not more than about 49% of said total duration, a stain removal effective amount of said enzyme-deactivating bleach; followed by (b) a step of releasing, in a second period starting at about 1 minute into said cycle and continuing for from about 30 sec. to the end of said cycle, at least one bleach scavenger capable of destroying said enzyme-deactivating bleach or of reacting therewith to form an enzyme-compatible bleach; and followed thereafter by (c) a step of releasing, in a third period starting at about 1 minute into said cycle and

continuing for from about 30 sec. to the end of said cycle, said detergent enzyme, and wherein further said release of detergent enzyme is delayed relative to the release of the bleach scavenger by a time sufficient to produce a cleaning-effective amount of said detergent enzyme.

5 All percentages and proportions herein are by weight, and all references cited are hereby incorporated by reference, unless otherwise specifically indicated.

BRIEF DESCRIPTION OF THE DRAWINGS

10 FIG. 1 is illustrative of a dissolution profile for a granular detergent composition for automatic dishwashing which is in conformity with the invention.

DETAILED DESCRIPTION OF THE INVENTION

15 As noted, dissolution profiles of detergent compositions herein are of great importance. In a highly preferred embodiment, the invention encompasses a detergent composition for use in a domestic automatic washing appliance, said detergent composition having granular form and further, having a dissolution profile wherein: (1) substantially all of said enzyme-deactivating bleach is released in a first period, starting at about 30 sec. or greater into, and ending at no more than about 49% of, the total duration of a single wash cycle of said appliance; (2) substantially all of said bleach scavenger is released in a second period, starting at about 1 min. or greater into said wash cycle, and (3) substantially
20 all of said detergent enzyme is released in a third period, starting at about 1 min. or greater into said wash cycle, but delayed relative to the release of the bleach scavenger by a time sufficient to provide a cleaning-effective amount of detergent enzyme.

25 Dissolution profiles in preferred terms can also be described with reference to disposal of enzyme-deactivating bleach before ingress of too much of the sensitive enzyme component. Thus in a preferred detergent, said dissolution profile is such that the concentration in water of enzyme-deactivating bleach not reacted with said bleach scavenger when the concentration of said detergent enzyme in water first reaches about 10% of said cleaning-effective amount, is less than about 0.2 ppm, preferably less than about 0.1 ppm, more preferably still less than about 0.05 ppm, most desirably, less than about 0.01 ppm.

Detergent Compositions

Detergent composition of the present invention comprise detergent enzymes, enzyme-deactivating bleaches, bleach scavengers and, in preferred embodiments, coating polymers.

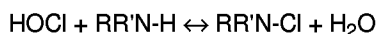
35 "Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a detergent composition. Preferred detergent enzymes are hydrolases such as proteases, amylases and lipases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types and improved types which, though more bleach compatible, have a remaining degree of bleach deactivation susceptibility.

40 "Enzyme-deactivating bleach", as used herein, refers specifically to any oxidizing bleach for which there is a measurable activity-reducing effect on detergent enzymes during normal use conditions, typically at pH's in the range from about 9 to about 12. Assay of detergent enzyme by conventional methods in presence of a bleach can be used to determine whether the bleach is "enzyme deactivating". Particularly strongly enzyme-deactivating bleaches include sodium hypochlorite, which can be liberated from any convenient source, such as sodium dichloroisocyanurate, as well as hypobromites and persulfates, especially monopersulfate.

45 The hereinbefore referenced Tivin patents identify perborate as an enzyme-incompatible bleach. Moreover the hereinbefore referenced EP 481,547 A suggests combining chlorine bleaches with perborate so as to improve bleaching. According to the present invention, perborate and other convenient sources of hydrogen peroxide (when used in a pH range of about 9 to about 12 in the instant detergent compositions) are not "enzyme-deactivating". In fact, for purposes of the present invention, they react chemically with, and destroy, hypochlorite and other enzyme-deactivating
50 bleaches herein. Thus, in general, hydrogen peroxide and other peroxides such as perborate or percarbonate are capable of acting as reducing agents, and in this model (desirably for the present invention) are examples of the essential bleach scavenger component further defined hereinafter. In another mode, they are capable of functioning as an optional, enzyme-compatible bleach herein, in which case they can be delivered to the wash after all enzyme-deactivating bleach has been destroyed. In a third aspect, a single aliquot of perborate or an equivalent hydrogen peroxide
55 source may be used in part as "bleach scavenger" and serve later, in-part, as an enzyme-compatible bleach.

"Bleach scavenger", as used herein, refers to any bleach-reactive compound which either destroys enzyme-deactivating bleach or converts it to a milder, enzyme-compatible form. Bleach scavengers may include compounds known in the art as chlorine scavengers or antioxidants. Certain preferred bleach scavengers for the present purposes may react irreversibly to destroy enzyme-deactivating bleach. Such is the case, for example, with sodium bisulfite as well as

the sodium perborates and sodium percarbonate. Other preferred bleach scavengers are selected from those which react reversibly according to the reaction:



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where the double-headed arrow indicates an equilibrium or reversible reaction. Highly preferred of such compounds are those which have small hydrolysis constants, i.e., compounds which, at a pH in the range from about 9 to about 12, bind hypochlorite strongly and thereby effectively limit the concentration of the sum of chlorine, hypochlorous acid and hypochlorite in the wash water. In this instance, a pronounced enzyme-compatibilizing effect can be obtained at more economical levels of the bleach scavenger. In contrast, when such compounds have large hydrolysis constants, i.e.,

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bind hypochlorite weakly, large excesses of the compound are required to effectively scavenge hypochlorite.

The present detergent compositions moreover comprise, in particles more fully defined hereinafter, one or more coating polymers, such as acrylate polymers or isophthalate polymers. Coating polymers herein are film-forming polymers useful to delay release of detergent enzyme for a time sufficiently delayed relative to the bleach scavenger, as described herein.

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In general, the instant detergent compositions may also comprise one or more additional materials, such as low foaming nonionic surfactants (especially useful in automatic dishwashing to control spotting/filming); builders which control calcium and/or magnesium and may have a buffering action, optionally with the further addition of water-soluble dispersants which modify and inhibit crystal growth of calcium and/or magnesium salts; alkalis to adjust pH; chelating agents which control transition metals; and additional bleach-modifying materials such as promoters in the form of bromide salts, bleach catalysts or bleach activators, provided that any such bleach-modifying materials are delivered in such a manner as to be compatible with the purposes of the present invention. The present detergent compositions may, moreover, comprise one or more conventional enzyme particle-making materials, including enzyme cores or "non-pareils", pigments, and the like, though in general, materials used for the production of particles herein are preferably checked for compatibility with spotting/filming on glassware. Test methods for spotting/filming are generally described in the automatic dishwashing detergent literature, including DIN test methods. Certain plasticizers, such as oily phthalates, especially at longer chain lengths, and insoluble materials such as clays, as well as long-chain fatty acids or soaps which form soap scum are preferably limited or excluded from the instant compositions when they are to be incorporated in automatic dishwashing compositions.

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Although, as noted, amounts of the essential ingredients can vary within wide ranges, preferred detergent compositions herein (which have a 1% aqueous solution pH of from about 9 to about 12) are those wherein (a) said stain-removal effective amount of said enzyme-deactivating bleach is sufficient to provide a maximum bleach concentration in water of from about 10 ppm to about 500 ppm, although concentrations in the order of about 100 ppm are typical; (b) said compatibilizing amount of said bleach scavenger is sufficient to at least equal about 70%, preferably about 80% or more, of the stoichiometric amount of said enzyme-deactivating bleach; and (c) said cleaning-effective amount of said detergent enzyme is sufficient to provide a detergent enzyme concentration in water of from about 0.0001 to about 500 ppm (more typical enzyme levels are low, as indicated hereinafter). The term "stoichiometric amount" refers to the amount required for a reaction between enzyme-deactivating bleach and bleach scavenger on a molar basis, as may be calculated from a writing of the chemical equation for the reaction.

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Enzyme-Deactivating Bleach

In general, any enzyme-deactivating bleach susceptible to the action of bleach scavengers may be used herein. Such bleaches are, in general, oxidizing bleaches rather than reducing bleaches, and do not include, as noted, the "amphoteric" bleach hydrogen peroxide. Preferred enzyme-deactivating bleaches for automatic dishwashing purposes are those which produce rapid and effective removal of tea and coffee stains from dishware. Preferred enzyme-deactivating bleaches include those selected from the group consisting of chlorine bleaches, bromine bleaches, persulfate bleaches and mixtures thereof. Persulfate bleaches, especially monopersulfate in any convenient form, such as OXONE as supplied by Dupont, are useful herein. More typically, chlorine bleaches or mixtures thereof with bromine bleaches will be used. Suitable chlorine bleaches are further illustrated and described in the hereinbefore referenced Kirk-Othmer review entitled "Bleaching Agents (Survey)", in Vol. 4, at pages 271-299, published in 1993 by John Wiley and Sons, New York, incorporated by reference. Preferred chlorine bleaches herein differ from chlorine itself both on account of generally alkaline environment and because of practical considerations.

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Thus preferred chlorine bleaches are illustrated by chlorinated trisodium phosphate and the chlorinated isocyanurates, especially sodium dichloroisocyanurate. To be noted, since rapid release of the enzyme-deactivating bleach is desired, it is preferred not to use the least soluble chlorine bleaches; for example the halogenated hydantoins tend to dissolve too slowly. Particles of enzyme-deactivating bleach may be used in smaller size fractions than those normally used in conventional formulations in order to improve the velocity of release. However, reduced particle size may affect

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storage stability. In order to offset this difficulty, coatings may be applied to the enzyme-deactivating bleach component. Coatings of bleaches have, as noted, been described in the art.

The invention is not limited to the use of chlorinated bleaches. Thus, in preferred embodiments, stain removal benefits may be enhanced by the addition of an N-Bromo compound or a bromide salt to the compositions.

Bleach Scavengers

Bleach scavengers suitable for use herein generally comprise at least one bleach-scavenging moiety. Such a moiety can be selected from the group consisting of reducing sulfur moieties, N-halo forming nitrogen moieties, reducing sugar moieties, peroxy moieties capable of acting as reducing agents, hydroxycarboxylate moieties, aminoalcohol moieties, and mixtures thereof. In alternate terms, bleach scavenging moieties herein can suitably be selected from the group consisting of ammonium, N-H - containing substituted ammonium, -NH₂, =NH, sulfamate, imidodisulfonate, glutamate, carbamate, cyanurate, isocyanurate, aminoacid, bisulfite, bisulfate, sulfite, thiosulfate, perborate, percarbonate, reducing sugar, ascorbate, malate, and mixtures thereof.

Highly preferred detergent compositions herein are those wherein said bleach scavenger is selected from the group consisting of ammonium sulfate, ammonium citrate and sodium bisulfite. Ammonium sulfate, ammonium thiosulfate, ammonium bisulfite, and sodium bisulfite are particularly preferred.

Preferably the bleach scavenger herein is a hydrophilic, rapid-dissolving, low molecular weight, nonhygroscopic, nondeliquescent solid compound. Such compounds can be non-charged, for example a reducing sugar; or may be ionic, in which case the active moiety can be the cation, as in ammonium sulfate or ammonium benzoate; the anion, as in sodium glutamate; or both, as in ammonium glutamate. Out of the many available bleach scavengers, liquid forms, such as certain liquid aminoalcohols, are not preferred. Also, in order that the bleach scavenger will dissolve and diffuse rapidly throughout the wash solution, the scavenger preferably has a molecular weight below about 2,000, preferably, below about 500, and is preferably not surface-active to a high degree. Typically, if surface-active, the bleach scavenger will have a critical micelle concentration in excess of about 10⁻² molar, preferably, in excess of about 10⁻¹ molar. Preferably, the bleach scavenger is therefore not a protein, although such substances have elsewhere been used as bleach scavengers and are inherently present in food soils. Suitably the bleach scavenger is selected from reducing inorganic scavengers, especially those which are sulfur-containing; reducing organic scavengers, such as reducing sugars; N-H functional compounds, especially ammonium salts, sulfamates, carbamates, cyanurates, isocyanurates, amino-acids; aromatic N-H functional amines; ascorbate; hydroxycarboxylic acids, especially malate; and enzyme-compatible redox bleaches which can act as reducing agents, such as sodium perborate (any convenient soluble solid-form source of hydrogen peroxide such as sodium percarbonate will suffice).

More preferably the bleach scavenger is selected from reducing sugars; ammonium citrate, ammonium sulfate, sulfamates; ascorbates; glutamates; aromatic N-H functional amines; sodium perborate monohydrate; and sodium percarbonate.

If desired, the bleach scavenger can have its mechanical properties modified, for example for binding purposes in a particle, by the inclusion of any inert substance which does not measurably spoil spotting/filming performance of the detergent.

In highly preferred detergents herein, said bleach scavenger is ammonium sulfate; optionally, said ammonium sulfate may have its binding properties modified, for example by a cellulose derivative.

In a granular detergent, bleach scavengers herein can be incorporated entirely within deterative enzyme-containing particles; or they may be divided into a portion which is incorporated with the enzyme into particles of a first kind and a portion which is incorporated into particles of a third kind (the enzyme-deactivating bleach being included in particles of a second kind). In general, particles of the third kind, when present, need to contain only bleach scavenger, preferably with coating materials such as the coating polymers used in particles of the first kind. Nonetheless, there may be added to any such particles one or more materials improving the mechanical handling characteristics, aesthetics etc.

Deterative Enzymes

In general, as noted, detergent compositions herein comprise one or more deterative enzymes. If only one enzyme is used, it is preferably an amyolytic enzyme when the composition is for automatic dishwashing use. Highly preferred for automatic dishwashing is a mixture of proteolytic enzymes and amyolytic enzymes.

In general, the enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders, etc. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated in the instant detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain

removal or soil removal effect on substrates such as fabrics, dishware and the like. Since enzymes are catalytic materials, such amounts may be very small. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 6%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For automatic dishwashing purposes, it may be desirable to increase the active enzyme content of the commercial preparations, in order to minimize the total amount of non-catalytically active materials delivered and thereby improve spotting/filming results.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S as ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

An especially preferred protease, 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, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/322,676, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having U.S. Serial No. 08/322,677, both filed October 13, 1994.

Amylases suitable herein include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo Industries.

Engineering of enzymes (e.g., stability-enhanced amylase) for improved stability, e.g., oxidative stability is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521. "Reference amylase" refers to a conventional amylase inside the scope of the amylase component of this invention. Further, stability-enhanced amylases, also within the invention, are typically compared to these "reference amylases".

The present invention, in certain preferred embodiments, can make use of amylases having improved stability in detergents, especially improved oxidative stability. A convenient absolute stability reference-point against which amylases used in these preferred embodiments of the instant invention represent a measurable improvement is the stability of TERMAMYL® in commercial use in 1993 and available from Novo Nordisk A/S. This TERMAMYL® amylase is a "reference amylase", and is itself well-suited for use in the ADD (Automatic Dishwashing Detergent) compositions of the invention, as well as in inventive fabric laundering compositions herein. Even more preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, all measured versus the above-identified reference-amylase. Preferred amylases herein can demonstrate further improvement versus more challenging reference amylases, the latter reference amylases being illustrated by any of the precursor amylases of which preferred amylases within the invention are variants. Such precursor amylases may themselves be natural or be the product of genetic engineering. Stability can be measured using any of the art-disclosed technical tests. See references disclosed in WO 94/02597, itself and documents therein referred to being incorporated by reference.

In general, stability-enhanced amylases respecting the preferred embodiments of the invention can be obtained from Novo Nordisk A/S, or from Genencor International.

Preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

As noted, "oxidative stability-enhanced" amylases are preferred for use herein despite the fact that the invention makes them "optional but preferred" materials rather than essential. Such amylases are non-limitingly illustrated by the following:

- (a) An amylase according to the hereinbefore incorporated WO/94/02597, Novo Nordisk A/S, published Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine (preferably threo-

nine), of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TER-MAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B.subtilis*, or *B.stearothermophilus*;

(b) Stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®;

(c) Particularly preferred herein are amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S. These amylases do not yet have a tradename but are those referred to by the supplier as QL37+M197T.

Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases.

Cellulases usable in, but not preferred, for the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful.

Suitable lipase enzymes for detergent use include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein. Another preferred lipase enzyme is the D96L variant of the native *Humicola lanuginosa* lipase, as described in WO 92/05249 and Research Disclosure No. 35944, March 10, 1994, both published by Novo. In general, lipolytic enzymes are less preferred than amylases and/or proteases for automatic dishwashing embodiments of the present invention.

Peroxidase enzymes can be used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are typically used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S. The present invention encompasses peroxidase-free automatic dishwashing composition embodiments.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

Coating Polymers

Preferred detergent compositions herein further include coating polymers, though these may be omitted when the invention is practiced in a different mode, for example as a method for dosing individual components into an automatic dishwasher. Suitable polymers herein are selected so that, as incorporated into enzyme particle coatings, they delay the disintegration or dissolution of the particle for specific time-periods. Suitable polymers are, for example, the same as, or preferably, variants of, those described in U.S. Patents 5,254,283 and 4,973,417; it should be appreciated that either the thickness of the polymer coating, or its dispersing properties, can be modified to accommodate the purposes of the invention. Polymer dispersing properties, to illustrate, are strongly influenced by hydrophobicity and molecular

weight, so that if, for example, an acrylate polymer is too hydrophilic, it may be copolymerized to provide, say, an ethacrylate or propacrylate rather than a methacrylate to increase hydrophobicity to the desired extent.

In preferred detergent compositions herein, the coating polymer is at least partially water-soluble at a pH in the range from about 5 to about 13.

In more detail, suitable coating polymers are selected from the group consisting of: modified cellulose polymers; acrylates, methacrylates, ethacrylates and their copolymers; polyethyleneglycols; film-forming polyesters; naturally derived gums; and mixtures thereof.

Polymers further illustrative of those useful herein include the following:

10

Name	Tradename	Description	Supplier
Hydroxypropyl methylcellulose (HPMC)	Methocel F50 Premium	Water soluble polymers derived from cellulose	Dow Chemicals
HPMC, PEG, Titanium Dioxide, Polysorbate 80	Opadry	A complete system for aqueous film coating	Colorcon
Ethylcellulose	Aquacoat ECD-30	Ethylcellulose Aqueous dispersion	FMC
Methacrylic acid and ethyl acrylate	Eudragit L 30D	Anionic copolymer in aqueous dispersion (enteric coating)	Rohm Pharma
Polyethylene Glycols (PEG)	same (except for Union Carbide name is Carbowax PEG)	PEG-200 PEG-400 PEG-600 PEG-1000 PEG-1450 PEG-3350 PEG-8000	Sigma, Chemax, Union Carbide
Carboxymethyl cellulose (CMC)	Carbose D72	Chloracetic acid on alkali cellulose	Penn Carbose
Carrageenan	NutricolGP 312 Konjac Powder	Konjac gum blend with Carrageenan	FMC
PVA (polyvinyl alcohols)	PVA 25	Polyvinyl Alcohol Based Product	ABCO
	Binder K1	Polyvinyl Based Product	ABCO

Carrageenan and similar materials may be used with good results. In addition, certain polyvinyl pyrrolidones and derivatives thereof may be used; such materials may also provide dye transfer inhibition benefits when used in the compositions.

Polymers heretofore known as soil release polymers, such as those referred to in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, U.S. Patent 3,959,230 to Hays, issued May 25, 1976, and U.S. Patent 3,893,929 to Basadur issued July 8, 1975, may be useful herein as coating polymer. See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S.

Patent 4,702,857, issued October 27, 1987 to Gosselink. Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters. In general, Soil Release Polymers are preferred as coating materials herein when the detergent composition is for use as a fabric laundering detergent.

5 In general, coating polymers herein may be used alone or in combination with any other compatible ingredients used in enzyme particle manufacture, for example pigments, provided that the level of such additives does not prevent the polymer from operating nor cause a spotting/filming deficiency. The coating layer may, of course, be the polymer alone, or at least consist essentially of said polymer without addition of other materials.

10 Although in the simplest embodiments it suffices to have a single coating layer in particles, multiple coatings, under-coatings, precoatings etc. are envisaged, provided that the sum total of the coatings provides the desired dissolution profile.

Preferably, polymer coatings herein, especially those used for particles of a first kind described in detail hereinafter, are applied by conventional Wurster fluidized bed coating processes.

15 Detergent Compositions Comprising Coated Particles

Detergent composition herein include those wherein there exist a plurality of particles of at least two distinct kinds. The term "plurality" of particles as used herein is used to distinguish preferred embodiments of this invention from tablets, where typically only one, two or a handful of large particles having sizes measured in millimeters or even centimeters are used. Tablets are not preferred herein.

20 Particles of a first kind herein each comprise one or more detergent enzymes, one or more bleach scavengers, surrounding or admixed with said detergent enzymes and one or more coating layers comprising a coating polymer and at least partially separating said detergent enzymes from at least a portion of said bleach scavengers.

25 The terms "surrounding or admixed with" are used to indicate that detergent enzyme does not come into contact with water before bleach scavenger, which would occur, for example, in the case of a two-sided tablet having bleach scavenger on one side and enzyme on the other. In highly preferred embodiments of the invention, there is always present at least some "surrounding" bleach scavenger or rapidly releasable bleach scavenger contained in particles of a third kind as further described hereinafter.

30 Particles of a second kind herein each comprise at least one enzyme deactivating bleach as described hereinbefore.

Additional particle types are also envisaged, especially particles of a third kind which comprise bleach scavenger without enzymes. These particles may be coated, for example to improve their mechanical handling characteristics, provided that the coating does not significantly impair the dissolution profile of the detergent. In general, from about 0.01 to about 1 weight fraction of said bleach scavenger may be incorporated into said particles of said first kind and from about 0.01 to about 1 weight fraction of said bleach scavenger is incorporated into said particles of said third kind.

Highly preferred detergent compositions for automatic dishwashing are those wherein all of said particles are substantially free from plasticizers, fatty acids, soaps and waxes having a measurable effect on spotting/filming.

35 In preferred detergent compositions herein, about 50% or more of said particles of said first and second kinds have a maximum dimension of no greater than about 2,000 micron; more preferably, particles of the first kind are based upon coating relatively small-sized enzyme cores, for example cores having a mean diameter of about 600 to about 650 micron and a relatively narrow size distribution. There is accordingly encompassed a detergent composition wherein about 50% or more, preferably about 80% or more of said particles of said first kind have a mean particle size in the range from about 400 micron to about 1000 micron.

45 Preferably, particles of said first kind have a disintegration rate of from about 1 (mg/(liter*min.)) to about 10 (mg/(liter*min.)) as measured at a pH of about 10 and a temperature of about 50 °C.

Fully-Formulated Detergent Composition

50 The present invention encompasses fully-formulated detergent compositions, including those for use in automatic dishwashing. Such compositions are nonlimitingly illustrated by those which comprise from about 0.1% to about 6%, preferably from about 0.2% to about 4% of said detergent enzyme; from about 0.2% to about 10%, preferably from about 0.5% to about 8% of said bleach scavenger; from about 0.2% to about 10%, preferably from about 0.5% to about 5% of said enzyme-deactivating bleach; and from about 0.01% to about 8% , preferably from about 0.1% to about 6% of said coating polymer. Such fully-formulated embodiments typically further comprise at least one low-foaming nonionic surfactant, at least one builder, at least one chelant and at least one dispersant, though additional or adjunct ingredients may be present.

Adjunct Ingredients

Even small quantities of greasy substances, including plasticizers, fatty acids soaps and waxes, may have adverse effects on spotting/filming in an automatic dishwashing operation, and may, moreover, carry insoluble or partially dissolved particles of detergent ingredients onto the glassware. In addition to low tolerance for greasy materials, there is typically, in automatic dishwashing, a rather low tolerance for particulate insoluble materials. Accordingly, such materials are preferably minimized when the present compositions are for automatic dishwashing use.

Deterative Surfactants --Surfactants are useful herein for their usual cleaning power and may be included in embodiments of the instant detergent compositions at the usual detergent-useful levels. In general, bleach-stable deterative surfactants are preferred.

Nonlimiting examples of surfactants useful herein include the conventional C₁₁-C₁₈ alkylbenzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"); the C₁₀-C₁₈ secondary alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium; unsaturated sulfates such as oleyl sulfate; the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS") especially those wherein x is from 1 to about 7; C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates); the C₁₀-C₁₈ glycerol ethers; the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides; and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. Deterative surfactants may be mixed in varying proportions for improved surfactancy as is well-known in the art. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxylate/propoxylates), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the cleaning compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be employed. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Automatic dishwashing compositions typically employ low sudsing surfactants, such as the mixed ethyleneoxy/propyleneoxy nonionics. Other conventional useful surfactants are listed in standard texts.

Low-Foaming Nonionic Surfactant - ADD (Automatic Dishwashing Detergent) 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 alkoxyated 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 (C₁₆-C₂₀ alcohol), preferably a C₁₈ 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, Buillot, 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 ethylenedi-

amine as initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and pro-
 oxylation of initiator compounds with a single reactive hydrogen atom, such as C₁₂₋₁₈ aliphatic alcohols, do not
 generally provide satisfactory suds control in the instant ADDs. Certain of the block polymer surfactant compounds desig-
 nated PLURONIC® and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD
 5 compositions of the invention.

A particularly preferred LFNI contains from about 40% to about 70% of a polyoxypropylene/polyoxyethylene/poly-
 oxypropylene block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of poly-
 oxyethylene 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 trimethylol-
 10 propane 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 prefera-
 bly 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 C₁₈ alcohol polyethoxylate, having a degree of ethoxylation of about 8,
 15 commercially available as SLF18 from Olin Corp., and any biodegradable LFNI having the melting point properties dis-
 cussed hereinabove.

Builders - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral
 hardness. Inorganic as well as organic builders can be used. Builders are typically used in automatic dishwashing and
 fabric laundering compositions, for example to assist in the removal of particulate soils.

20 The level of builder can vary widely depending upon the end use of the composition and its desired physical form.
 When present, the compositions will typically comprise at least about 1% builder. High performance compositions typi-
 cally comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent
 builder. Lower or higher levels of builder, however, are not excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and
 25 alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy poly-
 meric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbon-
 ates), sulfates, and aluminosilicates. However, non-phosphate builders are required in some locales. Compositions
 herein function surprisingly well even in the presence of "weak" builders (as compared with phosphates) such as citrate,
 or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders. See U.S. Pat. 4,605,509
 30 for examples of preferred aluminosilicates.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range
 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May
 12, 1987 to H. P. Rieck. NaSKS-6® is a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein
 as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 is the δ-
 35 Na₂SiO₅ form of layered silicate and can be prepared by methods such as those described in German DE-A-3,417,649
 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such
 as those having the general formula NaMSi_xO_{2x+1} · yH₂O wherein M is sodium or hydrogen, x is a number from 1.9 to
 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from
 Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the α-, β- and γ- forms. Other silicates may also be useful,
 40 such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing
 agent for oxygen bleaches, and as a component of suds control systems.

Silicates useful in automatic dishwashing (ADD) applications include granular hydrous 2-ratio silicates such as BRI-
 TESIL® H20 from PQ Corp., and the commonly sourced BRITESIL® H24 though liquid grades of various silicates can
 be used when the ADD composition has liquid form. Within safe limits, sodium metasilicate or sodium hydroxide alone
 45 or in combination with other silicates may be used in an ADD context to boost wash pH to a desired level.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent
 Application No. 2,321,001 published on November 15, 1973. Various grades and types of sodium carbonate and
 sodium sesquicarbonate may be used, certain of which are particularly useful as carriers for other ingredients, espe-
 cially deterative surfactants.

Aluminosilicate builders may be used in the present compositions though are not preferred for automatic dishwash-
 ing detergents. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular deter-
 gent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate
 builders include those having the empirical formula: [M_z(zAlO₂)_y] · xH₂O wherein z and y are integers of at least 6, the
 molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystal-
 line or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for
 producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October
 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the
 designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred laundry embodiment, the

crystalline aluminosilicate ion exchange material has the formula: $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O}$ wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter. Individual particles can desirably be even smaller than 0.1 micron to further assist kinetics of exchange through maximization of surface area. High surface area also increases utility of aluminosilicates as adsorbents for surfactants, especially in granular compositions. Aggregates of silicate or aluminosilicate particles may be useful, a single aggregate having dimensions tailored to minimize segregation in granular compositions, while the aggregate particle remains dispersible to submicron individual particles during the wash. As with other builders such as carbonates, it may be desirable to use zeolites in any physical or morphological form adapted to promote surfactant carrier function, and appropriate particle sizes may be freely selected by the formulator.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt or "overbased". When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine-tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty laundry detergent and automatic dishwashing formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in combination with zeolite, the aforementioned BRITESIL types, and/or layered silicate builders. Oxydisuccinates are also useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C_5 - C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylysuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylysuccinate (preferred), 2-pentadecenylysuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also U.S. Patent 3,723,322.

Fatty acids, e.g., C_{12} - C_{18} monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing in laundry compositions, which may need to be taken into account by the formulator. Fatty acids or their salts are undesirable in Automatic Dishwashing (ADD) embodiments in situations wherein soap scums can form and be deposited on dishware.

Where phosphorus-based builders can be used, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used though such materials are more commonly used in a low-level mode as chelants or stabilizers.

Chelating Agents

The compositions herein may also optionally contain one or more transition-metal selective sequestrants or "chelating agents", e.g., iron and/or copper and/or manganese chelating agents. Chelating agents suitable for use herein can be selected from the group consisting of aminocarboxylates, phosphonates (especially the aminophosphonates), polyfunctionally-substituted aromatic chelating agents, and mixtures thereof. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to control iron, copper and manga-

nese in washing solutions; other benefits include inorganic film prevention or scale inhibition. Commercial chelating agents for use herein include the DEQUEST® series, and chelants from Monsanto, DuPont, and Nalco, Inc.

Aminocarboxylates useful as optional chelating agents are further illustrated by ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetrapropionates, triethylenetetraamine-hexacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof. In general, chelant mixtures may be used for a combination of functions, such as multiple transition-metal control, long-term product stabilization, and/or control of precipitated transition metal oxides and/or hydroxides.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzene such as 1,2-dihydroxy-3,5-disulfobenzene.

A highly preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially (but not limited to) the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins. The trisodium salt is preferred though other forms, such as magnesium salts, may also be useful.

Aminophosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include the ethylenediaminetetrakis (methylene phosphonates) and the diethylenetriaminepentakis (methylene phosphonates). Preferably, these aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

If utilized, chelating agents or transition-metal-selective sequestrants will preferably comprise from about 0.001% to about 10%, more preferably from about 0.05% to about 1% by weight of the compositions herein.

Optional Bleach Adjuncts

(a) Bleach catalysts - If desired, detergent compositions herein may additionally incorporate a catalyst or accelerator to further improve bleaching. Any suitable bleach catalyst can be used. Typical bleach catalysts comprise a transition-metal complex, often one wherein the metal co-ordinating ligands are quite resistant to lability. Such catalyst compounds often have features of naturally occurring compounds but are principally provided synthetically and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; preferred examples of these catalysts include $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(PF_6)_2$, $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_2$, $Mn^{IV}_4(u-O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$, $Mn^{III}\text{-}Mn^{IV}_4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_3$, $Mn^{IV}\text{-}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})\text{-}(OCH_3)_3(PF_6)$, and mixtures thereof, though alternate metal-co-ordinating ligands as well as mononuclear complexes are also possible and monometallic as well as di- and polymetallic complexes, and complexes of alternate metals such as iron are all within the present scope. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Said manganese can be precomplexed with ethylenediaminedisuccinate or separately added, for example as a sulfate salt, with ethylenediaminedisuccinate. (See U.S. Application Ser. No. 08/210,186, filed March 17, 1994.) Other preferred transition metals in said transition-metal-containing bleach catalysts include iron or copper.

As a practical matter, and not by way of limitation, the bleaching compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 50 ppm, or less, of the catalyst species in the wash liquor.

(b) Bleach Activators - "Bleach activators" herein are optional materials herein, typified by TAED (tetra-acetyl ethylenediamine). Numerous such activators are known. Various nonlimiting examples of such activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. Nonanoyloxybenzene sulfonate (NOBS) or acyl lactam activators may be used, and mixtures thereof with TAED can also be used. See also U.S. 4,634,551 for other typical conventional bleach activators. Also known are amido-derived bleach activators of the formulae: $R^1N(R^5)C(O)R^2C(O)L$ or $R^1C(O)N(R^5)R^2C(O)L$ wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group other than an alpha-modified lactam. Further illustration of bleach activators of the above formulae include (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551. Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990. Still another class of bleach activators includes acyl lactam activators such as octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl

valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. The present compositions can optionally comprise acyl benzoates, such as phenyl benzoate, or known quaternary substituted bleach activators (QSBA). QSBA's are further illustrated in U.S. 4,539,130, Sept. 3, 1985 and U.S. Pat. No. 4,283,301. British Pat. 1,382,594, published Feb. 5, 1975, discloses a class of QSBA's optionally suitable for use herein. U.S. 4,818,426 issued Apr. 4., 1989 discloses another class of QSBA's. Also see U.S. 5,093,022 issued March 3, 1992 and U.S. 4,904,406, issued Feb. 27, 1990. Additionally, QSBA's are described in EP 552,812 A1 published July 28, 1993, and in EP 540,090 A2, published May 5, 1993.

(c) Organic Peroxides, especially Diacyl Peroxides - These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. Dibenzoyl peroxide is preferred.

Other Ingredients

Detergent ingredients or adjuncts optionally included in the instant compositions can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics of the compositions. Such materials are further illustrated in U.S. Pat. No. 3,936,537, Baskerville et al. Adjuncts which can also be included in compositions of the present invention, in their conventional art-established levels for use (generally from 0% to about 20% of the detergent ingredients, preferably from about 0.5% to about 10%), include other active ingredients such as dispersant polymers from BASF Corp. or Rohm & Haas; color speckles, anti-tarnish and/or anti-corrosion agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, enzyme stabilizing agents, perfumes, solubilizing agents, clay soil removal/anti-redeposition agents, carriers, processing aids, pigments, solvents for liquid formulations, fabric softeners, static control agents, solid fillers for bar compositions, etc. Dye transfer inhibiting agents, including polyamine N-oxides such as polyvinylpyridine N-oxide can be used. Dye-transfer-inhibiting agents are further illustrated by polyvinylpyrrolidone and copolymers of N-vinyl imidazole and N-vinyl pyrrolidone. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, typically, 0.1%-2%, for example to provide additional suds and to enhance grease removal performance.

Brightener

Any optical brighteners, fluorescent whitening agents or other brightening or whitening agents known in the art can be incorporated in the instant compositions when they are designed for fabric treatment or laundering, at levels typically from about 0.05% to about 1.2%, by weight, of the detergent compositions herein.

pH and Buffering Variation

Many detergent compositions herein will be buffered, i.e., they are relatively resistant to pH drop in the presence of acidic soils. However, other compositions herein may have exceptionally low buffering capacity, or may be substantially unbuffered. Techniques for controlling or varying pH at recommended usage levels more generally include the use of not only buffers, but also additional alkalis, acids, pH-jump systems, dual compartment containers, etc., and are well known to those skilled in the art. Detergent compositions herein in granular form typically limit water content, for example to less than about 7% free water, for best storage stability.

Storage stability of detergent compositions can be further enhanced by limiting the content in the compositions of adventitious redox-active substances such as rust and other traces of transition metals in undesirable form. Certain compositions may moreover be limited in their total halide ion content, or may have any particular halide, e.g., bromide, substantially absent. Bleach stabilizers such as stannates can be added for improved stability and formulations may be substantially nonaqueous if desired.

Methods

The present invention also encompasses a method for compatible staged release of an enzyme-deactivating bleach followed by one or more detergent enzymes in an aqueous washing process in a domestic washing appliance having at least one wash cycle of finite total duration, comprising (a) a step of releasing, in a first period starting at about 30 sec. into said cycle and finishing at a time which is not more than about 49% of said total duration, a stain removal effective amount of said enzyme-deactivating bleach; followed by (b) a step of releasing, in a second period starting at about 1 minute into said cycle and continuing for from about 30 sec. to the end of said cycle, at least one bleach scav-

enger capable of destroying said enzyme-deactivating bleach or of reacting therewith to form an enzyme-compatible bleach; and followed thereafter by (c) a step of releasing, in a third period starting at about 1 minute into said cycle and continuing for from about 30 sec. to the end of said cycle, said detergent enzyme, and wherein further said release of detergent enzyme is delayed relative to the release of the bleach scavenger by a time sufficient to produce a cleaning-effective amount of said detergent enzyme. While this method preferably utilizes compositions according to the present invention, it is to be recognized that depending on the features of the dishwashing machine used, multiple solid and/or liquid compositions released by the machine according to a sequence of the present method may also be employed.

Preferably in said method, said detergent enzyme release exceeds about 50% of the total of said detergent enzyme no sooner than about 2 minutes into a wash cycle of said appliance.

In more detail, said method can be carried out in aqueous solution wherein: said domestic washing appliance is a U.S., European or Japanese automatic dishwasher; said total duration is from about 3 minutes to about 3 hours; said wash cycle is isothermal or temperature-varying, at temperatures of from about 5 °C to about 95 °C; a sum of the maximum concentrations of all released ingredients is from about 200 ppm to about 10,000 ppm, expressed on the basis of a single water fill of said appliance; and said release steps are further characterized in that, when the concentration of said detergent enzyme in water first reaches about 10% of the total of said detergent enzyme released, the unreacted concentration of said enzyme-deactivating bleach is less than about 0.2 ppm.

Highly preferred is a method wherein: said domestic washing appliance is a U.S. automatic dishwasher; said total duration is from about 3 minutes to about 30 minutes; said wash cycle is a warm-fill cycle attaining a maximum water temperature of no more than about 70°C; a sum of the maximum concentrations of all released ingredients is from about 800 ppm to about 4,000 ppm, and said release steps are further characterized in that, when the concentration of said detergent enzyme in water first reaches about 10% of the total of said detergent enzyme released, the unreacted concentration of said enzyme-deactivating bleach is less than about 0.05 ppm.

The aforementioned method may of course comprise additional steps, preceding said steps, of (1) charging said appliance with food-soiled dishware; (2) adding to a dispenser cup of said appliance a formulated granular detergent product comprising each of said enzyme-deactivating bleach, bleach scavenger and detergent enzyme ingredients together with builders and alkali sufficient to bring the wash pH to within the range from about 9 to about 12; and (3) initiating a conventional wash cycle of said appliance. More preferably still, said first period has a total duration of about 5 min. or less; the total amount of said enzyme-deactivating bleach is sufficient to provide a concentration in water of from about 20 ppm to about 250 ppm, said concentration being calculated on the basis of no reaction with bleach scavenger; said second period starts at about 1 min. into, and ends about two minutes before the end of said wash cycle; said bleach scavenger is released in an amount sufficient to equal at least 80% of the concentration required for complete stoichiometric reaction of said bleach scavenger with said enzyme-deactivating bleach; and said third period starts at about 2 min. into, and ends at about the end of said wash cycle.

EXAMPLE 1

The following fully-formulated granular automatic dishwashing detergents are prepared by mixing:

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Example 1	A	B
INGREDIENTS	wt %	wt %
Particles of Type 1 (Enzyme, Scavenger, Coating Polymer)	6	6
Particles of Type 2 (Bleach, as Sodium Dichloroisocyanurate)	6	7
Builder: Trisodium Citrate Dihydrate (anhydrous basis)	10	20
Builder: Sodium Carbonate (anhydrous basis)	20	10
Silicate: BRITESIL H ₂ O®, PQ Corp. (as SiO ₂)	12	8
Chelant: Diethylenetriaminepentaacetic Acid, Sodium Salt	0	0.1
Chelant: Ethylenediamine Disuccinate, Trisodium Salt	0.3	0
Chelant: Hydroxyethylidiphosphonate (HEDP), Sodium Salt	0	0.5
Dispersant (See Note 1)	6	8
Nonionic Surfactant (See Note 2))	2	2
Sodium Sulfate, water, minors	Balance to 100%	Balance to 100%
Note 1: One or more of: Sokolan PA30®, BASF or Accusol 480N®, Rohm & Haas. Note 2: SLF18®, Olin Corp. or LF404®, BASF.		

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Particles of Type 1 for the above compositions are made as follows:

A Uni-Glatt laboratory fluidized bed spray coater (Wurster) is charged with about 300g of a simple co-granulate of Savinase® 12T and Termamyl® 60T, from Novo. The co-granulate comprises 20% ammonium sulfate, by weight, and has an average diameter of about 650 µm. These particles are coated with about 75 g of a methacrylic acid copolymer (Eudragit L30D®, Rohm Pharma GmbH, Darmstadt, Germany) by spraying with 500 g of the following composition:

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	Parts by Weight
Eudragit L30D	1000
Propanediol	30
Talc	70
Antifoam emulsion	2
Water	898
Total Parts by Weight	<u>2000</u>

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Spraying is at a rate of about 5 ml/min. at an inlet temperature of from about 40 °C to about 60 °C and an outlet temperature in the range from about 30 °C to about 40 °C.

Particles of Type 2 for the above compositions are particles of Sodium Dichloroisocyanurate, obtainable from Olin Corp., having particle diameters of from about 400 to about 1000 µm.

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EXAMPLE 2

The following fully-formulated granular automatic dishwashing detergents are prepared by mixing:

Example 2	A	B
INGREDIENTS	wt %	wt %
Particles of Type 1 (Enzyme, Scavenger, Coating Polymer)	2	4
Particles of Type 2 (Bleach, as Sodium Dichloroisocyanurate)	6	7
Particles of Type 3 (Additional Scavenger)	0.5	2
Builder: Trisodium Citrate Dihydrate (anhydrous basis)	10	20
Builder: Sodium Carbonate (anhydrous basis)	20	10
Silicate: BRITESIL H2O®, PQ Corp. (as SiO ₂)	12	8
Chelant: Diethylenetriaminepentaacetic Acid, Sodium Salt	0	0.1
Chelant: Ethylenediamine Disuccinate, Trisodium Salt	0.3	0
Chelant: Hydroxyethyldiphosphonate (HEDP), Sodium Salt	0	0.5
Dispersant (See Note 1)	6	8
Nonionic Surfactant (See Note 2))	2	2
Sodium Sulfate, water, minors	Balance to 100%	Balance to 100%
Note 1: One or more of: Sokolan PA30®, BASF, Accusol 480N®, Rohm & Haas. Note 2: SLF18®, Olin Corp. or LF404®, BASF.		

Particles of Type 1 for the above compositions are made as follows:

A Uni-Glatt laboratory fluidized bed spray coater (Wurster) is charged with about 300g of Protease D-loaded cores from Genencor further comprising 5% ammonium sulfate, by weight added by the supplier, these cores having an average diameter of about 650 µm. These particles are coated with about 85 g of a methacrylic acid copolymer (Eudragit L30D®, Rohm Pharma GmbH, Darmstadt, Germany) by spraying with 567 g of the following composition:

	Parts by Weight
Eudragit L30D	1000
Propanediol	30
Talc	70
Antifoam emulsion	2
Water	898
Total Parts by Weight	<u>2000</u>

Spraying is at a rate of about 5 ml/min. at an inlet temperature of from about 40 °C to about 60 °C and an outlet temperature in the range from about 30 °C to about 40 °C.

Particles of Type 2 for the above compositions are particles of Sodium Dichloroisocyanurate, obtainable from Olin Corp., having particle diameters of from about 400 to about 1000 µm.

Particles of Type 3 for the above compositions are made as follows:

A Uni-Glatt laboratory fluidized bed spray coater (Wurster) is charged with about 300g of ammonium sulfate particles (about 60% by weight ammonium sulfate, 40% minors), having an average diameter of about 650 µm. These particles are coated with about 75 g of a methacrylic acid copolymer (Eudragit L30D®, Rohm Pharma GmbH, Darmstadt, Germany) by spraying with 567 g of the following composition:

	Parts by Weight
Eudragit L30D	1000
Propanediol	30
Talc	70
Antifoam emulsion	2
Water	898
Total Parts by Weight	<u>2000</u>

15 Spraying is at a rate of about 5 ml/min. at an inlet temperature of from about 40 °C to about 60 °C and an outlet temperature in the range from about 30 °C to about 40 °C.

The above examples are of course illustrative, and are not intended to be limiting of the invention. The present invention has additional ramifications and embodiments, thus there is provided within the spirit and scope of the invention an improvement in a method for washing domestic dishware in an automatic dishwashing appliance using an enzyme and an enzyme-deactivating bleach. The improvement comprises releasing into the water present in a cycle of said appliance first said enzyme-deactivating bleach, followed by a bleach-compatibilizing amount or excess thereof of a bleach scavenger, followed by said detergent enzyme; provided that the total period for which said detergent enzyme is present in said water exceeds the period for which said bleach is present in enzyme-deactivating form. Achieving this method is in no way limited to the particular granular embodiments shown. Thus, liquid forms of ingredients could be used and delivered, for example, in an automatic dishwashing appliance employing a conventional timed delivery mechanism to provide precisely the release profile indicated in Fig. 1. The present invention accordingly provides numerous advantages to the consumer, such as excellent removal of tea stains, starchy soil removal, excellent spotlessness and lack of film on both glasses and dishware, excellent silvercare, and economy.

30 Claims

1. A detergent composition for the release of bleach followed by enzyme, said composition comprising:

- (a) at least one enzyme-deactivating bleach;
 (b) at least one bleach scavenger; and
 (c) at least one detergent enzyme;

and wherein further, upon mixing with water, said detergent composition begins releasing: (i) a stain-removal effective amount of said enzyme-deactivating bleach, followed by (ii) a compatibilizing amount of said bleach scavenger, followed thereafter by (iii) a cleaning-effective amount of said detergent enzyme.

2. A detergent composition according to Claim 1 for use in a washing appliance, said detergent composition having granular form and further having a dissolution profile releasing substantially all of said stain-removal effective amount of said enzyme-deactivating bleach in no more than the first 75% of a wash cycle of said appliance.

3. A detergent composition according to either of Claims 1 or 2 having the form of a granular automatic dishwashing detergent for use in a domestic automatic dishwashing appliance wherein further said detergent composition has a dissolution profile releasing more than 50% of said cleaning-effective amount of said detergent enzyme no sooner than 2 minutes into a wash cycle of said appliance.

4. A detergent composition according to any of Claims 1-3 wherein further said dissolution profile releases more than 50% of said compatibilizing amount of said bleach scavenger no sooner than 1 minute into a wash cycle of said appliance.

5. A detergent composition according to any of Claims 1-4 for use in a domestic automatic washing appliance, said detergent composition having granular form and further having a dissolution profile wherein:

- (i) substantially all of said enzyme-deactivating bleach is released in a first period, starting at 30 sec. or greater into, and ending at no more than 49% of, the total duration of a single wash cycle of said appliance;

(ii) substantially all of said bleach scavenger is released in a second period, starting at 1 min. or greater into said wash cycle, and further wherein

(iii) substantially all of said detergent enzyme is released in a third period, starting at 1 min. or greater into said wash cycle, and wherein further said release of detergent enzyme is delayed relative to the release of the bleach scavenger by a time sufficient to provide a cleaning-effective amount of said detergent enzyme.

6. A detergent composition comprising:

(a) a plurality of particles of a first kind, each comprising:

- (i) one or more detergent enzymes,
- (ii) one or more bleach scavengers, surrounding or admixed with said detergent enzymes, and
- (iii) one or more coating layers comprising a coating polymer and at least partially separating said detergent enzymes from at least a portion of said bleach scavengers;

(b) a plurality of particles of a second kind, each comprising at least one enzyme-deactivating bleach; and

(c) optionally, a plurality of particles of a third kind, each comprising an additional amount of bleach scavenger and being substantially free from said detergent enzyme;

whereby, when said detergent composition is dispensed into water in an automatic dishwashing appliance, the concentration of said enzyme-deactivating bleach is reduced to less than 1 ppm prior to the release of no more than 50% of said detergent enzyme, on a weight basis.

7. A detergent composition according to any of Claims 1-6 wherein said enzyme-deactivating bleach is selected from the group consisting of chlorine bleaches, bromine bleaches, persulfate bleaches and mixtures thereof.

8. A detergent composition according to any of Claims 1-7 wherein said detergent enzyme is selected from the group consisting of amylases, proteases, lipases, and mixtures thereof.

9. A detergent composition according to any of Claims 1-8 wherein said bleach scavenger comprises a bleach-scavenging moiety selected from the group consisting of ammonium, N-H - containing substituted ammonium, -NH₂, =NH, sulfamate, imidodisulfonate, glutamate, carbamate, cyanurate, isocyanurate, aminoacid, bisulfite, bisulfate, sulfite, thiosulfate, perborate, percarbonate, reducing sugar, ascorbate, malate, and mixtures thereof, and preferably selected from the group consisting of ammonium sulfate, ammonium thiosulfate, ammonium citrate, ammonium bisulfite, sodium bisulfite, and mixtures thereof.

10. A detergent composition according to any of Claims 1-9 comprising a coating polymer selected from the group consisting of modified cellulose polymers; acrylates, methacrylates, ethacrylates and their copolymers; polyethyleneglycols; film-forming polyesters; naturally derived gums; and mixtures thereof.

11. A method for compatible staged release of an enzyme-deactivating bleach followed by one or more detergent enzymes in an aqueous washing process in a domestic washing appliance having at least one wash cycle of finite total duration, said method comprising (a) a step of releasing, in a first period starting at 30 sec. into said cycle and finishing at a time which is not more than 49% of said total duration, a stain removal effective amount of said enzyme-deactivating bleach; followed by (b) a step of releasing, in a second period starting at 1 minute into said cycle and continuing for from 30 sec. to the end of said cycle, at least one bleach scavenger capable of destroying said enzyme-deactivating bleach or of reacting therewith to form an enzyme-compatible bleach; and followed thereafter by (c) a step of releasing, in a third period starting at 1 minute into said cycle and continuing for from 30 sec. to the end of said cycle, said detergent enzyme, and wherein further said release of detergent enzyme is delayed relative to the release of the bleach scavenger by a time sufficient to produce a cleaning-effective amount of said detergent enzyme.