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Remarks:

A request for correction of the description has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 3.).

(54) **Machine dishwashing composition containing amphoteric polymers**

(57) A composition and method of preventing lime soap deposition on tableware cleaned in a machine dishwasher are described. The detergent composition contains an effective amount of an amphoteric polymer and a lipolytic enzyme as described.

**EP 0 835 925 A2**

**Description****Field of Invention**

5 The invention relates to detergent compositions containing amphoteric polymers to control the deposition of lime soap, particularly machine dishwashing compositions containing lipolytic enzymes.

**Background of the Invention**

10 A critical criteria for an effective machine dishwashing composition is the appearance of both the washed glassware and plastic articles to the consumer. Spotting and filming of such tableware, when washed with commercial products, generally results from mineral deposition during the evaporation of undrained wash solution in the drying step. The deposited minerals are from many sources, including salts of ingredients in the product formulations, calcium carbonate from temporary water hardness, and suspended soil.

15 The deposition on the surfaces of the washed articles make them look dull due to the presence of spots, streaks or surface covering film. The most intense spotting problems are related to the deposition of hydrophobic soil fragments. In the final rinse stage, this hydrophobic soil is thought to break-up the water film, leaving droplets behind on the tableware which result in mineral deposits observed as white spots upon evaporation of the water component.

20 A prior art solution to the removal of these white mineral spots has been the addition of a rinse aid composition to the rinsing water of the machine cycle. Although the visual appearance of the washed tableware is improved, some spotting, but especially mineral film formation has still been observed even with the use of this additional product. Moreover, use of a rinse aid is inconvenient to the consumer.

25 The major fraction of the hydrophobic soil fragments that are present on washed tableware is believed to be triglyceride and fatty ester soil. Consequently, machine dishwashing and rinse aid compositions incorporating lipolytic enzymes which assist in breaking down these soils have been described in EP-A-346,136 and EP-A-271,155. Although lipolytic enzymes can reduce the formation of mineral spots due to hydrophobic soil fragments, the enzymes can also cause a different type of white deposits to build up on hydrophobic surfaces such as plastics. These fatty deposits are due to precipitation of lime soaps which are formed from the mixture of calcium and magnesium ions in the wash water with fatty acids, which are liberated from the triglyceride and fatty ester soils by the action of the lipolytic enzymes. The higher the level of fatty soil present in the dishwasher, the worse the problem of lime soap deposition.

30 Prior art solutions to these problems include formulations of machine dishwashing compositions incorporating certain lime soap dispersants with lipolytic enzymes as described in WO-94/07984 and WO-94/07985 (Proctor & Gamble). Tableware washed with compositions containing lipases and these lime soap dispersants have been observed to have low lime soap film scores (i.e. little to no filming is observed). However, a large number of white mineral spots on the washed articles have been observed. It is thus believed that the lime soap dispersants described in these publications actually inhibit the action of the lipase.

35 Hydrophobically modified copolymers, of especially acrylic acid, have been described in copending Gordon et al.; U.S. Serial No. 08/457,690 for incorporation in machine dishwashing compositions. Calcium soap deposition is reduced by the presence of these polymers.

40 US-A-4,891,149 describes polymeric lime soap dispersants which consist of copolymers and water soluble salts of copolymers of acrylic acid, methacrylic acid and mixtures thereof and acrylamide, alkyl or alkylol substituted acrylamide, or mixture of said acrylamides. Optionally, enzymes may also be added to the formulations.

45 US-A-5,308,532 (Rohm & Haas) describes aminoacryloyl - containing terpolymers which are useful for reducing mineral spotting and filming of tableware. Thus, the detergent formulation acts by preventing hydrophobic deposits on glassware and does not address the issue of preventing lime soap deposition. The use of lipolytic enzymes in combination with such terpolymers to control the deposition of lime soaps is neither taught nor suggested.

It is therefore an object of the present invention to provide machine dishwashing compositions and methods of using them to prevent lime soap deposition on washed tableware.

50 Another object of the invention is to selectively combine lipolytic enzymes with particular amphoteric polymers in a detergent composition to control lime soap deposition and virtually prevent spotting and lime soap filming on cleaned tableware.

**Summary of the Invention**

55 Accordingly, the present invention provides a machine washing composition comprising:

(a) an effective amount of a amphoteric polymer wherein in a 1% aqueous wash liquor having a pH of about 7 or greater, positive charges on the polymer comprise between 1% and 50%, preferably between 2% and 20%, most

preferably between 5 and 15% of the total charges on the polymer having a formula selected from:

5 i)  $A_x B_y C_z$  where in a 1% aqueous wash liquor pH A is an anionic moiety, B is a cationic moiety and C is an anionic, cationic, amphoteric or uncharged moiety and mixtures thereof, x, y, and z refer to mole percentages, x is 50-99%, preferably 80-98%, most preferably 85-95%, and y is 1-50%, preferably 2-20%, most preferably 5-15% and z is 0 to 25%, preferably 0 to 18%; or

10 ii)  $D_d E_f$  where at the wash pH D is an amphoteric moiety, E is an anionic, cationic, or uncharged moiety and mixture thereof, d and f refer to mole percentages, and d is 1-100% and f is 0-99% provided the above stated charge distribution is satisfied;

15 (b) 0.01% to about 4 wt. % of a lipolytic enzyme; and

(c) about 1 to about 75% by wt. of a builder material.

A bleaching agent is optionally included.

### Detailed Description of Preferred Embodiments

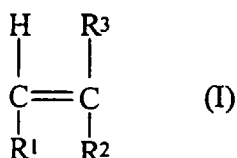
20 The amphoteric polymers incorporated in the compositions of the invention are present in an effective amount, preferably about 0.1 to about 25%, more preferably from about 1 to about 15%, most preferably from about 2 to about 10% by wt.

25 Wash pH is defined as the measured pH of a 1% aqueous solution of dishwasher water in the main wash cycle after addition and dissolution of the detergent composition. At a wash pH preferably between about 7 and about 12, most preferably between about 8 and about 11, positive charges on the polymer comprise between 1% and 50%, preferably between 2% and 20%, most preferably between 5 and 15% of the total charges on the polymer.

The amphoteric polymers are addition polymers which may be prepared by (1) copolymerizing selected monomers which are anionic at the wash pH with selected monomers which are cationic at the wash pH, or (2) by polymerizing selected amphoteric monomers.

30 A first means of preparing the amphoteric polymers which are useful in the invention consists of copolymerizing from about 50 to about 99%, preferably from about 80 to about 98%, most preferably from about 85 to about 98% by wt. of the anionic monomer (A) with about 1 to about 50%, preferably from about 2 to about 20%, most preferably from about 2 to about 15% by wt. of the cationic monomer. Optionally, a charged or uncharged moiety (C) is also copolymerized.

35 The monomers (A) used to prepare the amphoteric polymers are substituted vinyl compounds which have anionic character at wash pH. Preferred monomers are substituted vinyl compounds of formula I

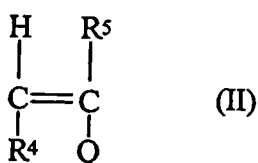


45 wherein  $R^1$ ,  $R^2$ , and  $R^3$  are independently a hydrogen,  $C_1$  to  $C_3$  alkyl, a carboxylate group or a carboxylate group substituted with a  $C_1$  to  $C_{30}$  straight or branched alkyl, aromatic heterocycle or a polyalkylamine oxide with the requirement that at least one of  $R^1$ ,  $R^2$ , or  $R^3$  must be a carboxylate or substituted carboxylate;

50 Preferred monomers include acrylic acid, methacrylic acid, maleic acid,  $\alpha$ -ethacrylic acid,  $\beta,\beta$ -dimethacrylic acid, methylenemalonic acid, vinylacetic acid, allylacetic acid, ethylideneacetic acid, propylideneacetic acid, crotonic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid and the like. Most preferred monomers include acrylic acid, methacrylic acid, and maleic acid.

The monomers (B) used to form the amphoteric polymers of the invention which have cationic character at wash pH are substituted vinyl compounds of formula II

5



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wherein  $\text{R}^4$  is a hydrogen, aromatic, heterocycle or a polyalkylamine oxide;  $\text{R}^5$  is a hydrogen or a  $\text{C}_1$  to  $\text{C}_{30}$  straight or branched alkyl; and  $\text{Q}$  is a nitrogen-containing organic radical, said radical having a  $\text{pK}_a$  value of  $> 7$ . methacrylate, dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylamide and dialkylaminoalkyl acrylamide.

15

The monomers of formula II are preferably quaternized wherein  $\text{Q}$  is preferably selected from the group consisting of formula III



20

wherein  $\text{X}^-$  is any suitable counterion such as halogen, hydroxide, sulfate, hydrosulfate, phosphate, formate and acetate or, a compound of formula IV



25

wherein  $\text{Z}$  is selected from the group consisting of  $\text{O}$ ,  $\text{COO}$  and  $\text{CONR}^{11}$  in which  $\text{R}^{11}$  is a hydrogen or a  $\text{C}_1$  to  $\text{C}_3$  alkyl group;  $\text{R}^6$  and  $\text{R}^7$  are each independently selected from the group consisting of hydrogen,  $\text{C}_1$  to  $\text{C}_4$  alkyl or  $\text{R}^6$  and  $\text{R}^7$  taken together form a  $\text{C}_3$  to  $\text{C}_7$  aliphatic heterocycle;  $m$  is 0 to 2 provided that when  $m$  is 0 a  $\text{C}-\text{N}$  bond is present in lieu of the  $(\text{CH}_2)_m$  group and  $\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  are each independently selected from a group consisting of hydrogen or a  $\text{C}_1$  to  $\text{C}_4$  alkyl; or  $\text{R}^8$  and  $\text{R}^9$  are taken together with the nitrogen to which they are attached to form a 3 to 7 membered non-aromatic nitrogen heterocycle; and  $\text{X}$  is any suitable counterion such as a halogen, hydroxide, sulfate, hydrosulfate, phosphate, formate and acetate.

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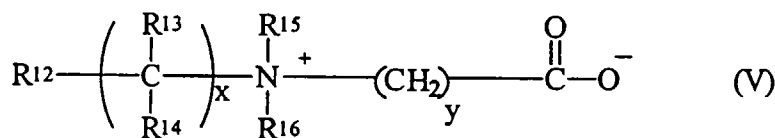
Preferred examples of the quaternized monomers are (3-acrylamidopropyl) trimethylammonium chloride (APTAC), (3-methacrylamidopropyl) trimethylammonium chloride (MAPTAC), and dimethyldiallylammonium chloride (DMDAC). Other suitable examples include such materials as vinylbenzyltrialkylammonium salts and the like.

35

Monomers (C) which are anionic or cationic are selected from compounds of formula I or II, respectively.

Amphoteric monomers (C) may be selected from compounds of formula V described below.

40



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wherein,  $\text{R}^{12}$  is a  $\text{C}_3$  to  $\text{C}_6$  monoethylenically unsaturated carboxylate;  $\text{R}^{13}$  and  $\text{R}^{14}$  each independently represent hydrogen or a  $\text{C}_1$  to  $\text{C}_3$  alkyl;  $\text{R}^{15}$  and  $\text{R}^{16}$  each independently represent a hydrogen or a  $\text{C}_1$  to  $\text{C}_3$  alkyl;  $x$  is 1 to 3; and  $y$  is 1 to 3.

50

Suitable carboxylates represented by  $\text{R}^{12}$  include, but are not limited to, acrylic acid, methacrylic acid,  $\alpha$ -ethacrylic acid,  $\beta,\beta$ -dimethacrylic acid, methylenemalononic acid, vinylacetic acid, allylacetic acid, ethylideneacetic acid, propylideneacetic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, and alkali metal ammonium salts thereof.

Preferably, the unsaturated carboxylic acid is acrylic or methacrylic acid.

55

Uncharged monomers (C) are selected from  $\text{C}_1$ - $\text{C}_4$  alkyl esters of acrylic acid, methacrylic acid, and itaconic acid;  $\text{C}_1$ - $\text{C}_4$  hydroxyalkyl esters of acrylic acid, methacrylic acid, and itaconic acid, alkylene oxide esters of acrylic acid, methacrylic acid, and itaconic acid having 1-20 alkylene oxide repeat units; and  $\text{C}_1$ - $\text{C}_{20}$  EO1-EO20 ethoxyalkyl esters of acrylic acid, methacrylic acid, and itaconic acid; styrene; vinyl alcohol; vinyl acetate; methyl vinyl ether; and allyl alco-

hols. Preferably the uncharged monomer is C1-C4 alkyl ester of acrylic acid, methacrylic acid, or itaconic acid, C1-C4 hydroxyalkyl ester of acrylic acid, methacrylic acid, or itaconic acid, or C1-C20 EO1-EO20 ethoxyalkyl ester of acrylic acid, methacrylic acid, or itaconic acid.

If these optional monomers (C) are present they should be present only in an amount of less than 25% of the total monomer distribution.

Preferably the amphoteric polymers ( $A_xB_yC_z$  wherein z is 0) produced from the monomers of formulas I and II are formed of monomers of acrylic acid polymerized with quaternized basic monomers.

A second means of obtaining amphoteric polymers useful in the invention is the polymerization of an amphoteric monomer (D) having a formula (V) as described above.

The amphoteric monomers of formula (V) may be homopolymerized or copolymerized with non-amphoteric polymerizable monomers (E) in an amount from about 0 to about 99% by wt., preferably from 0 to about 75% by wt., with the requirement that the previously defined polymer charge distribution be satisfied.

Suitable anionic, and cationic monomers from which the moiety E is selected are represented by formulas I and II. Uncharged monomers are selected from C1-C4 alkyl esters of acrylic acid, methacrylic acid, and itaconic acid; C1-C4 hydroxyalkyl esters of acrylic acid, methacrylic acid, and itaconic acid, alkylene oxide esters of acrylic acid, methacrylic acid, and itaconic acid having 1-20 alkylene oxide repeat units; and C1-C20 EO1-EO20 ethoxyalkyl esters of acrylic acid, methacrylic acid, and itaconic acid; styrene; vinyl alcohol; vinyl acetate; methyl vinyl ether; and allyl alcohols. Preferably the uncharged monomer is C1-C4 alkyl ester of acrylic acid, methacrylic acid, or itaconic acid, C1-C4 hydroxyalkyl ester of acrylic acid, methacrylic acid, or itaconic acid, or C1-C20 EO1-EO20 ethoxyalkyl ester of acrylic acid, methacrylic acid, or itaconic acid.

Suitable examples of amphoteric polymers include, but are not limited to, a copolymer of acrylic acid and 3-acrylamidopropyl trimethylammonium chloride as described in EP-A- 560, 519 Rohm and Haas, and EXP-2072 and EXP-2075 (terpolymers of acrylic acid, dimethyldiallylammonium chloride and C14-20 EO 20 itaconate ester available from Alco). Preferably, the polymers are the copolymers of acrylic acid and 3-acrylamido-propyl trimethylammonium chloride.

### Lipolytic Enzymes

Lipolytic enzymes are an essential component of the machine washing compositions of the invention. They are present at levels of active enzyme of from 0.01 to 4% by wt., preferably 0.01% to 3% by wt., most preferably from 0.05% to 1.5% by wt. of the composition, based on lipolytic activity of 100 LU/mg. Lipolytic activity is commonly defined by the amount of titratable fatty acid liberated from triglyceride under specified conditions. One lipase unit (LU) of activity is equivalent to liberation of one micromole of butyric acid per minute from an emulsion of tributyrin and gum arabic in the presence of  $Ca^{++}$  and NaCl at 30 Deg. C and pH 7.

Lipases facilitate the degradation or alteration of soils and stains comprising triglycerides or fatty esters. Lipases suitable for use herein include those of animal, plant and microbiological origin. Suitable lipases are also found in many strains of bacteria and fungi. For example, lipases suitable for use herein can be obtained from Pseudomonas, Aspergillus, Staphylococcus, Toxins, Mycobacterium Tuberculosis, Mycotorula Lipolytica and Sclerotinia microorganisms. Lipases from chemically or genetically modified mutants are also included herein. Mixtures of lipase from various strains are also included herein.

Suitable animal lipases are found in the body fluids and organs of many species. A preferred class of animal lipase herein are the pancreatic lipases.

A preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in EP-A-0258068, which is commercially available from Novo Industri A/S, Denmark, under the tradename Lipolase.

Tradenames of other suitable lipases are Lipomax, ex. Gist Brocades (now Genencor), the Netherlands and Lipase G-1000, ex. Solvay Enzymes, USA.

### Hypohalite Bleaching Agent

Hypohalite may be used as long as the bleach is added to avoid deactivation of the enzymes of the formulation. A preferred method of preventing enzyme deactivation is encapsulation of the bleach is described in US-A-5,200,236, herein incorporated by reference. In the patented method, the bleaching agent is encapsulated as a core in a paraffin wax material having a melting point from about 40°C to 50°C. The wax coating has a thickness of from 100 to 1500 microns.

Suitable reactive chlorine or bromine oxidizing materials are chloro and bromo amides such as trichloroisocyanuric, tribromoisocyanuric, dibromoisocyanuric and dichloroisocyanuric acids, and salts thereof with water solubilizing cations such as potassium and sodium. Hydantoin compounds such as 1,3-dichloro-5,5-dimethylhydantoin are also quite suit-

able.

### **Peroxy Bleaching Agents**

5 The oxygen bleaching agents of the compositions include organic peroxy acids and diacylperoxides. Typical monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxy acids such as:

10 i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g., peroxy-alpha-naphthoic acid, and magnesium monoperoxyphthalate

15 ii) aliphatic and substituted aliphatic monoperoxy acids, e.g., peroxyauric acid, epsilon-phthalimido-peroxyhexanoic acid and o-carboxybenzamido peroxyhexanoic acid, N-nonylamidoperadipic acid and N-nonylamidopersuccinic acid.

20 iii) Cationic peroxyacids such as those described in US-A-5,422,028, US-A-5,294,362; and US-A-5,292,447, Atty. Docket No. 95-0394-UNI; Case 7392, Oakes et al.; and U.S. S/N 08/210,973, Oakes et al., herein incorporated by reference.

25 iv) Sulfonyl peroxyacids such as compounds described in US-A-5,039,447 (Monsanto Co.), herein incorporated by reference.

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryl diperoxy acids, such as:

30 v) 1,12-diperoxydodecanedioic acid

vi) 1,9-diperoxyazelaic acid

vii) diperoxybrassylic acid; diperoxysecacic acid and diperoxy-isophthalic acid

viii) 2-decyldiperoxybutan-1,4-dioic acid

ix) N,N<sup>1</sup>-terephthaloyl-di(6-aminopercaproic acid).

35 A typical diacylperoxide useful herein includes dibenzoylperoxide.

Inorganic peroxygen compounds are also suitable for the present invention. Examples of these materials useful in the invention are salts of monopersulfate, perborate monohydrate, perborate tetrahydrate, and percarbonate.

40 Preferred oxygen bleaching agents include epsilon-phthalimido-peroxyhexanoic acid, o-carboxybenzaminoperoxyhexanoic acid, and mixtures thereof. Most preferred bleaching agents include perborate monohydrate and percarbonate.

The oxygen bleaching agent is present in the composition in an amount from about of 1 to 20 weight percent, preferably 1 to 15 weight percent.

The oxygen bleaching agent may be incorporated directly into the formulation or may be encapsulated by any number of encapsulation techniques known in the art to produce stable capsules in alkaline liquid formulations.

### **Bleach Precursors**

45 Suitable peroxygen peracid precursors for peroxy bleach compounds have been amply described in the literature, including GB Nos. 836,988; 855,735; 907,356; 907,358; 907,950; 1,003,310 and 1,246,339; US-A-3,332,882 and US-A-4,128,494.

50 Typical examples of precursors are polyacylated alkylene diamines, such as N,N,N<sup>1</sup>,N<sup>1</sup>-tetraacetylene diamine (TAED) and N,N,N<sup>1</sup>,N<sup>1</sup>-tetraacetylmethylene diamine (TAMD); acylated glycolurils, such as tetraacetylglycoluril (TAGU); triacetylcyanurate, sodium sulfophenyl ethyl carbonic acid ester, sodium acetyloxybenzene sulfonate (SABS), sodium nonanoyloxy benzene sulfonate (SNOBS) and choline sulfophenyl carbonate. Peroxybenzoic acid precursors are known in the art, e.g., as described in GB-A-836,988. Examples of suitable precursors are phenylbenzoate; phenyl p-nitrobenzoate; o-nitrophenyl benzoate; o-carboxyphenyl benzoate; p-bromophenylbenzoate; sodium or potassium benzoyloxy benzene-sulfonate; and benzoic anhydride.

Preferred peroxygen bleach precursors are sodium p-benzoyloxybenzene sulfonate, N,N,N<sup>1</sup>,N<sup>1</sup>-tetraacetylene diamine, sodium nonanoyloxybenzene sulfonate and choline sulfophenyl carbonate.

55 Bleach catalysts which may also be used in the detergent compositions include manganese catalysts such as those described in US-A-5,246,621.

**Detergent Builder Materials**

The compositions of this invention contains either organic builders, particularly carboxylates, or inorganic builders, particularly phosphorous containing compounds.

**Phosphorus Containing Builders**

Examples of phosphorus-containing inorganic builders include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates and polyphosphates, particularly ammonium and alkanol ammonium salts, and phosphonates. Particularly preferred phosphate builders include sodium and potassium triphosphates, pyrophosphates, hexametaphosphates and trimetaphosphates. When phosphate builders are incorporated into the formula, they are present in an amount of about 10 to about 75% by wt., most preferably 15 to about 60 wt. %.

**Nonphosphorus Inorganic Builders**

Non-phosphorus-containing inorganic builders may be additionally used such as water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, layered silicates such as SKS-6 ex Hoechst, metasilicates, phytic acid, borate and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates, including layered silicates and zeolites.

**Organic Builders**

Organic detergent builders useful in the present invention include a variety of polycarboxylate compounds. As used herein "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least three (3) carboxylates. Monomeric or polymeric carboxylates are preferred. Examples of organic builders include alkali metal citrates, succinates, malonates, fatty acid sulfonates, fatty acid carboxylates, nitrilotriacetates, phytates, phosphonates, alkanehydroxyphosphonates, oxydisuccinates, alkyl and alkenyl disuccinates, oxydiacetates, carboxymethoxy succinates, ethylenediamine tetraacetates, tartrate monosuccinates, tartrate disuccinates, tartrate monoacetates, tartrate diacetates, oxidized starches, oxidized heteropolymeric polysaccharides, and polyhydroxysulfonates.

Polycarboxylates include polyacrylates, polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/poly-maleate and polyacrylate/ polymethacrylate copolymers, acrylate/maleate/vinyl alcohol terpolymers, aminopolycarboxylates and polyacetal carboxylates, and polyaspartates and mixtures thereof. Such carboxylates are described in US-A-4,144,226, US-A-4,146,495 and US-A-4,686,062, herein incorporated by reference.

Alkali metal citrates, nitrilotriacetates, oxydisuccinates, polyphosphonates and acrylate/maleate copolymers and acrylate/maleate/vinyl alcohol terpolymers are especially preferred organic builders.

When the builder is comprised primarily of either monomeric or polymeric carboxylates or mixtures thereof the builder should be present in an amount of 10 to 60 wt. %, most preferably 15 to 50 wt. %.

The foregoing detergent builders are meant to illustrate but not limit the types of builders that can be employed in the present invention.

**Enzymes**

Additional enzymes capable of facilitating the removal of soils from a substrate may also be present in an amount of up to about 10% by wt., preferably 1 to about 5 wt. %. Such enzymes include proteases (e.g., Alcalase<sup>®</sup>, Savinase<sup>®</sup> and Esperase<sup>®</sup> from Novo Industries A/S and Purafect OxP<sup>®</sup>, ex. Genencor) and amylases (e.g., Termamyl<sup>®</sup> and Duramyl<sup>®</sup> from Novo Industries and Purafect OxAm<sup>®</sup>, ex. Genencor).

**Optional Ingredients**

Minor amounts of various other components may optionally be present in the cleaning composition. These include filler, non-carboxylic thickening agents, defoamer, bleach scavengers including but not limited to sodium bisulfite, reducing sugars, and short chain alcohols; solvents and hydrotropes such as ethanol, isopropanol and xylene sulfonates; enzyme stabilizing agents; soil suspending agents; antiredeposition agents; anti-corrosion agents, such as benzotriazole and isocyanuric acid described in US-A-5,374,369; ingredients to enhance decor care such as certain aluminum salts described in U.S. Serial No. 08/444,502 and 08/444,503, herein incorporated by reference; colorants; perfumes; opacifiers such as titanium dioxide; and other functional additives.

**Sequestrants**

The detergent compositions herein may also optionally contain one or more transition metal (such as Fe, Mn, or Cu) chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein. 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 remove transition metal ions such as Fe, Mn, and Cu from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates; N-hydroxyethylethylenediaminetriacetates; nitrilotriacetates; ethylenediamine tetrapropionates; triethylenetetraaminehexaacetates; diethylenetriaminepentaacetates; ethylenediamine disuccinate; ethanoldiglycines; alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Phosphonates and amino phosphonates 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 ethylenediaminetetrakis (methylenephosphonates), nitrilotris (methylenephosphonates) and diethylenetriaminepentakis (methylenephosphonates).

Preferably, these phosphonates and aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See US-A-3,812,044, Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such composition.

**Anti-Scalants**

Scale formation on dishes and machine parts is an important problem that needs to be resolved or at least mitigated in formulating a machine warewashing product, especially in the case of low-phosphate (e.g. less than the equivalent of 20% by weight, particularly 10% by weight of sodium triphosphate) and phosphate-free machine warewashing compositions, particularly zero-P machine warewashing compositions.

In order to reduce this problem, co-builders, such as polyacrylic acids or polyacrylates (PAA), acrylate/maleate copolymers, polyaspartates, ethylenediamine disuccinate and the various organic polyphosphonates, e.g. Dequest series, may be incorporated in one or more system components. For improved biodegradability, (as such co-builders), the block co-polymers of formula (I) as defined in published PCT patent specification WO 94/17170 may also be used.

In any component, the amount of anti-scalant may be in the range of from 0.5 to 10, preferably from 0.5 to 5, and more preferably from 1 to 5% by weight.

**Surfactants**

Useful surfactants include anionic, nonionic, cationic, amphoteric, amphoteric types and mixtures of these surface active agents. It is understood that surfactants should be selected and used at such levels as conventionally known in the art so as not to deactivate enzymes in the formula. Such surfactants are well known in the detergent art and are described at length in "Surface Active Agents and Detergents", Vol. II, by Schwartz, Perry & Birch, Interscience Publishers, Inc. 1959, herein incorporated by reference.

Surfactants, if present in the composition, may be selected from the following:

**Anionic surfactants**

Anionic synthetic detergents can be broadly described as surface active compounds with one or more negatively charged functional groups. An important class of anionic compounds are the water-soluble salts, particularly the alkali metal salts, of organic sulfur reaction products having in their molecular structure an alkyl radical containing from about 6 to 24 carbon atoms and a radical selected from the group consisting of sulfonic and sulfuric acid ester radicals.

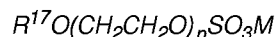
*Primary Alkyl Sulfates*



where  $R^{17}$  is a primary alkyl group of 8 to 18 carbon atoms and M is a solubilizing cation. The alkyl group  $R^{17}$  may

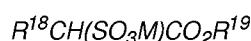
have a mixture of chain lengths. It is preferred that at least two thirds of the  $R^{17}$  alkyl groups have a chain length of 8 to 14 carbon atoms. This will be the case if  $R^{17}$  is coconut alkyl, for example. The solubilizing cation may be a range of cations which are in general monovalent and confer water solubility. Alkali metal, notably sodium, is especially envisaged. Other possibilities are ammonium and substituted ammonium ions, such as trialkanolammonium or trialkylammonium.

#### Alkyl Ether Sulfates



where  $R^{17}$  is a primary alkyl group of 8 to 18 carbon atoms,  $n$  has an average value in the range from 1 to 6 and  $M$  is a solubilizing cation. The alkyl group  $R^{17}$  may have a mixture of chain lengths. It is preferred that at least two thirds of the  $R^{17}$  alkyl groups have a chain length of 8 to 14 carbon atoms. This will be the case if  $R^{17}$  is coconut alkyl, for example. Preferably  $n$  has an average value of 2 to 5.

#### Fatty Acid Ester Sulfonates



where  $R^{18}$  is an alkyl group of 6 to 16 atoms,  $R^{19}$  is an alkyl group of 1 to 4 carbon atoms and  $M$  is a solubilizing cation. The group  $R^{18}$  may have a mixture of chain lengths. Preferably at least two thirds of these groups have 6 to 12 carbon atoms.

This will be the case when the moiety  $R^{18}CH(-)CO_2(-)$  is derived from a coconut source, for instance. It is preferred that  $R^{19}$  is a straight chain alkyl, notably methyl or ethyl.

#### Alkyl Benzene Sulfonates

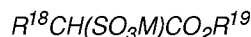


where  $R^{20}$  is an alkyl group of 8 to 18 carbon atoms,  $Ar$  is a benzene ring ( $C_6H_4$ ) and  $M$  is a solubilizing cation. The group  $R^{20}$  may be a mixture of chain lengths. Straight chains of 11 to 14 carbon atoms are preferred.

Organic phosphate based anionic surfactants include organic phosphate esters such as complex mono- or diester phosphates of hydroxyl- terminated alkoxide condensates, or salts thereof. Included in the organic phosphate esters are phosphate ester derivatives of polyoxyalkylated alkylaryl phosphate esters, of ethoxylated linear alcohols and ethoxylates of phenol.

Also included are nonionic alkoxyates having a sodium alkylencarboxylate moiety linked to a terminal hydroxyl group of the nonionic through an ether bond. Counterions to the salts of all the foregoing may be those of alkali metal, alkaline earth metal, ammonium, alkanolammonium and alkylammonium types.

Particularly preferred anionic surfactants are the fatty acid ester sulfonates with formula:



where the moiety  $R^{18}CH(-)CO_2(-)$  is derived from a coconut source and  $R^{19}$  is either methyl or ethyl.

### **Nonionic surfactants**

Nonionic surfactants can be broadly defined as surface active compounds with one or more uncharged hydrophilic substituents. A major class of nonionic surfactants are those compounds produced by the condensation of alkylene oxide groups with an organic hydrophobic material which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Illustrative, but not limiting examples, of various suitable nonionic surfactant types are:

*polyoxyethylene or polyoxypropylene condensates of aliphatic carboxylic acids, whether linear- or branched-chain and unsaturated or saturated, containing from about 8 to about 18 carbon atoms in the aliphatic chain and incorpo-*

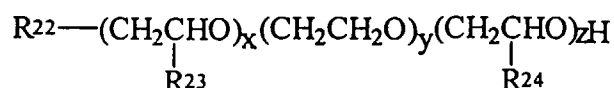
rating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable carboxylic acids include "coconut" fatty acids (derived from coconut oil) which contain an average of about 12 carbon atoms, "tallow" fatty acids (derived from tallow-class fats) which contain an average of about 18 carbon atoms, palmitic acid, myristic acid, stearic acid and lauric acid,

*polyoxyethylene or polyoxypropylene condensates of aliphatic alcohols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to about 24 carbon atoms and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable alcohols include "coconut" fatty alcohol, "tallow" fatty alcohol, lauryl alcohol, myristyl alcohol and oleyl alcohol.*

Ethoxylated fatty alcohols may be used alone or in admixture with anionic surfactants, especially the preferred surfactants above. The average chain lengths of the alkyl group  $R^{21}$  in the general formula:  $R^{21}O(CH_2CH_2O)_nH$  is from 6 to 24 carbon atoms. Preferably the group  $R^{21}$  may have chain lengths in a range from 9 to 18 carbon atoms.

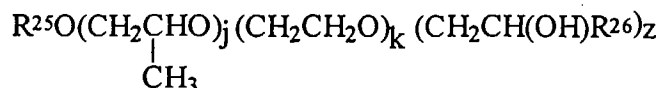
The average value of  $n$  should be at least 2. The numbers of ethylene oxide residues may be a statistical distribution around the average value. However, as is known, the distribution can be affected by the manufacturing process or altered by fractionation after ethoxylation. Particularly preferred ethoxylated fatty alcohols have a group  $R^{21}$  which has 9 to 18 carbon atoms while  $n$  is from 2 to 8.

Also included within this category are nonionic surfactants having a formula:



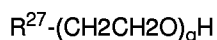
wherein  $R^{22}$  is a linear alkyl hydrocarbon radical having an average of 6 to 18 carbon atoms,  $R^{23}$  and  $R^{24}$  are each linear alkyl hydrocarbons of about 1 to about 4 carbon atoms,  $x$  is an integer of from 1 to 6,  $y$  is an integer of from 4 to 20 and  $z$  is an integer from 4 to 25.

One preferred nonionic surfactant of the above formula is Poly-Tergent SLF-18<sup>®</sup> a registered trademark of the Olin Corporation, New Haven, Conn. having a composition of the above formula where  $R^{22}$  is a  $C_6$ - $C_{10}$  linear alkyl mixture,  $R^{23}$  and  $R^{24}$  are methyl,  $x$  averages 3,  $y$  averages 12 and  $z$  averages 16. Another preferred nonionic surfactant is



wherein  $R^{25}$  is a linear, aliphatic hydrocarbon radical having from about 4 to about 18 carbon atoms including mixtures thereof; and  $R^{26}$  is a linear, aliphatic hydrocarbon radical having from about 2 to about 26 carbon atoms including mixtures thereof;  $j$  is an integer having a value of from 1 to about 3;  $k$  is an integer having a value from 5 to about 30; and  $z$  is an integer having a value of from 1 to about 3. Most preferred are compositions in which  $j$  is 1,  $k$  is from about 10 to about 20 and  $z$  is 1. These surfactants are described in WO 94/22800. Other preferred nonionic surfactants are linear fatty alcohol alkoxylates with a capped terminal group, as described in U.S. 4,340,766 to BASF.

Another nonionic surfactant included within this category are compounds of formula:



wherein  $R^{27}$  is a  $C_6$ - $C_{24}$  linear or branched alkyl hydrocarbon radical and  $q$  is a number from 2 to 50; more preferably  $R^{27}$  is a  $C_8$ - $C_{18}$  linear alkyl mixture and  $q$  is a number from 2 to 15.

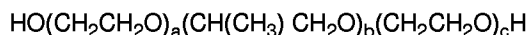
*polyoxyethylene or polyoxypropylene condensates of alkyl phenols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to 12 carbon atoms and incorporating from about 2 to about 25 moles of ethylene oxide and/or propylene oxide.*

*polyoxyethylene derivatives of sorbitan mono-, di-, and tri-fatty acid esters wherein the fatty acid component has between 12 and 24 carbon atoms. The preferred sorbitan trilaurate, sorbitan monopalmitate, sorbitan tripalmitate,*

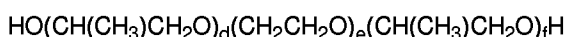
sorbitan monostearate, sorbitan monoisostearate, sorbitan tripalmitate, sorbitol tristearate, sorbitan monooleate, and sorbitan trioleate. The polyoxyethylene chains may contain between about 4 and 30 ethylene oxide units, preferably about 10 to 20. The sorbitan ester derivatives contain 1, 2 or 3 polyoxyethylene chains dependent upon whether they are mono-, di- or tri-acid esters.

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*polyoxyethylene-polyoxypropylene block copolymers* having formula:



10 or

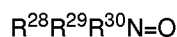


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wherein a, b, c, d, e and f are integers from 1 to 350 reflecting the respective polyethylene oxide and polypropylene oxide blocks of said polymer. The polyoxyethylene component of the block polymer constitutes at least about 10% of the block polymer. The material preferably has a molecular weight of between about 1,000 and 15,000, more preferably from about 1,500 to about 6,000. These materials are well-known in the art. They are available under the trademark "Pluronic" and "Pluronic R", a product of BASF Corporation.

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*Amine oxides* having formula:



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wherein  $\text{R}^{28}$ ,  $\text{R}^{29}$  and  $\text{R}^{30}$  are saturated aliphatic radicals or substituted saturated aliphatic radicals. Preferable amine oxides are those wherein  $\text{R}^{28}$  is an alkyl chain of about 10 to about 20 carbon atoms and  $\text{R}^{29}$  and  $\text{R}^{30}$  are methyl or ethyl groups or both  $\text{R}^{28}$  and  $\text{R}^{29}$  are alkyl chains of about 6 to about 14 carbon atoms and  $\text{R}^{30}$  is a methyl or ethyl group.

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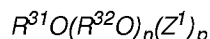
*Amphoteric synthetic detergents* may also be broadly described as derivatives of aliphatic and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contain from about 8 to about 18 carbons and one contains an anionic water-solubilizing group, i.e., carboxy, sulpho, sulphato, phosphato or phosphono. Examples of compounds falling within this definition are sodium 3-dodecylamino propionate and sodium 2-dodecylamino propane sulfonate.

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*Amphoteric synthetic detergents* can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium and sulphonium compounds in which the aliphatic radical may be straight chained or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulpho, sulphato, phosphato or phosphono. These compounds are frequently referred to as betaines. Besides alkyl betaines, alkyl amino and alkyl amido betaines are encompassed within this invention.

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*Alkyl Glycosides*



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wherein  $\text{R}^{31}$  is a monovalent organic radical (e.g., a monovalent saturated aliphatic, unsaturated aliphatic or aromatic radical such as alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl, aryl, alkylaryl, hydroxyalkylaryl, arylalkyl, alkenylaryl, arylalkenyl, etc.) containing from about 6 to about 30 (preferably from about 8 to 18 and more preferably from about 9 to about 13) carbon atoms;  $\text{R}^{32}$  is a divalent hydrocarbon radical containing from 2 to about 4 carbon atoms such as ethylene, propylene or butylene (most preferably the unit  $(\text{R}^{32}\text{O})_n$  represents repeating units of ethylene oxide, propylene oxide and/or random or block combinations thereof); n is a number having an average value of from 0 to about 12;  $\text{Z}^1$  represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms (most preferably a glucose unit); and p is a number having an average value of from 0.5 to about 10 preferably from about 0.5 to about 5.

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Examples of commercially available materials from Henkel Kommanditgesellschaft Aktien of Dusseldorf, Germany include APG<sup>®</sup> 300, 325 and 350 with  $\text{R}^{31}$  being  $\text{C}_9\text{-C}_{11}$ , n is 0 and p is 1.3, 1.6 and 1.8-2.2 respectively; APG<sup>®</sup> 500 and 550 with  $\text{R}^{31}$  is  $\text{C}_{12}\text{-C}_{13}$ , n is 0 and p is 1.3 and 1.8-2.2, respectively; and APG<sup>®</sup> 600 with  $\text{R}^{31}$  being  $\text{C}_{12}\text{-C}_{14}$ , n is

0 and p is 1.3.

While esters of glucose are contemplated especially, it is envisaged that corresponding materials based on other reducing sugars, such as galactose and mannose are also suitable.

The amount of surfactant present in the final formula should be from about 0.5 to about 30% by weight of the composition. The preferred range of surfactant is from 0.5 to 20% by weight, more preferably from 0.5 to 10% by weight.

### **Filler**

An inert filler material which is water-soluble may also be present in cleaning compositions. This material should not precipitate calcium or magnesium ions at the filler use level. Suitable for this purpose are organic or inorganic compounds. Organic fillers include sucrose esters and urea. Representative inorganic fillers include sodium sulfate, sodium chloride and potassium chloride. A preferred filler is sodium sulfate. Its concentration may range from 0% to 20%, preferably from about 2% to about 10% by weight of the cleaning composition.

### **Thickeners & Stabilizers**

Thickeners are often desirable for liquid cleaning compositions. Thixotropic thickeners such as smectite clays including montmorillonite (bentonite), hectorite, saponite, and the like may be used to impart viscosity to liquid cleaning compositions. Silica, silica gel, and aluminosilicate may also be used as thickeners. Salts of polyacrylic acid (of molecular weight of from about 300,000 up to 6 million and higher), including polymers which are cross-linked may also be used alone or in combination with other thickeners. Use of clay thickeners for machine dishwashing compositions is disclosed for example in US-A-4,431,559; US-A-4,511,487; US-A-4,740,327; US-A-4,752,409. Commercially available synthetic smectite clays include Laponite supplied by Laporte Industries. Commercially available bentonite clays include Korthix H and VWH ex Combustion Engineering, Inc.; Polargel T ex American Colloid Co.; and Gelwhite clays (particularly Gelwhite GP and H) ex English China Clay Co. Polargel T is preferred as imparting a more intense white appearance to the composition than other clays. The amount of clay thickener employed in the compositions is from 0.1 to about 10%, preferably 0.5 to 5%. Use of salts of polymeric carboxylic acids is disclosed for example in GB-A-2,164,350, US-A-4,859,358 and US-A-4,836,948.

For liquid formulations with a "gel" appearance and rheology, particularly if a clear gel is desired, a chlorine-resistant polymeric thickener is particularly useful. US-A-4,260,528 discloses natural gums and resins for use in clear machine dishwashing detergents, which are not chlorine stable. Acrylic acid polymers that are cross-linked manufactured by, for example, B.F. Goodrich and sold under the trade name "Carbopol" have been found to be effective for production of clear gels, and Carbopol 940, 617 and 627, having a molecular weight of about 4,000,000 are particularly preferred for maintaining high viscosity with excellent chlorine stability over extended periods. Further suitable chlorine-resistant polymeric thickeners are described in US-A-4,867,896 incorporated by reference herein.

The amount of thickener employed in the compositions is from 0 to 5%, preferably 0.5-3%.

Stabilizers and/or co-structurants such as long-chain calcium and sodium soaps and C<sub>12</sub> to C<sub>18</sub> sulfates are detailed in US-A- 3,956,158 and US-A-4,271,030 and the use of other metal salts of long-chain soaps is detailed in US-A-4,752,409. Other co-structurants include Laponite and metal oxides and their salts as described in US-A-4,933,101, herein incorporated by reference. The amount of stabilizer which may be used in the liquid cleaning compositions is from about 0.01 to about 5% by weight of the composition, preferably 0.01-2%. Such stabilizers are optional in gel formulations. Co-structurants which are found especially suitable for gels include trivalent metal ions at 0.01-4% of the compositions, Laponite and/or water-soluble structuring chelants at 0.01-5%. These co-structurants are more fully described in the US-A-5,141,664, hereby incorporated by reference.

### **Defoamer**

The formulations of the cleaning composition comprising surfactant may further include a defoamer. Suitable defoamers include mono-and distearyl acid phosphate, silicone oil and mineral oil. Even if the cleaning composition has only defoaming surfactant, the defoamer assists to minimize foam which food soils can generate.

The compositions may include 0.02 to 2% by weight of defoamer, or preferably 0.05-1.0%. Preferred antifoam systems are described in Angevaare et al.; US S/N 08/539,923, herein incorporated by reference.

The following examples will serve to distinguish this invention from the prior art and illustrate its embodiments more fully. Unless otherwise indicated, all parts, percentages and proportions referred to are by weights.

### **Example 1**

The lime soap dispersant properties of amphoteric polymers within the scope of the invention was compared to that

of lime soap dispersants known in the prior art as described below.

The polymers were evaluated for their lime soap dispersing power value (LSDP), which is a conventional measurement of the effectiveness of a material for dispersing lime soap. The lime soap dispersing power value (LSDP) is defined as the (weight ratio of dispersant to sodium oleate X 100) based on the amount of dispersant required to disperse lime soap curd formed by 0.025g sodium oleate and 30mls of water of 333 ppm. CaCO<sub>3</sub> equivalent hardness. According to the test, a low LSDP value is an indication of an effective lime soap dispersant. A detailed description of the test is found in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil Chem. Soc., 27, pages 88-90, (1950). The materials used in the comparison are described in Table I below:

Table 1

MATERIALS	SOURCE	LSDP
Amphoteric Polymer	PC2 Supplied by Rohm & Haas	1.5
Amphoteric Polymer	E-2072 Supplied By ALCO	1.5
Amphoteric Polymer	E-2075 Supplied By ALCO	2.5
C13-C15 Alcohol Ethoxylate (12EO)	Described in WO 94/07985	6.0
C12-C18 Alcohol Ethoxy Sulfate (3EO)	Described in WO 94/07985	4.0
Polyacrylic Acid (200,000 MW)		22.0
Polyacrylic Acid (4,500 MW)	Acusol 445 supplied by Rohm and Haas	15.0
Polyacrylic Acid/Acrylamide (200,000 MW)	Supplied by Aldrich	17.5

As this example illustrates, amphoteric polymers within the scope of the invention are extremely effective lime soap dispersants in comparison to similar polymers outside the scope of the invention and in comparison to the preferred lime soap dispersants claimed in WO 94/07984 and WO 94/07985

Example 2

The effect on glass and plasticware appearance of polymers and surfactants having an LSDP of less than 8 were compared by determining the effectiveness of each material in preventing the formation of mineral spots and films on clear glass tumblers and inhibition of lime soap filming on polyethylene plates when incorporated into the lipase containing base formulation.

A base machine dishwashing detergent composition was prepared as described in Table 2 below.

Table 2

INGREDIENTS	% BY WT.
STPP	51.0
Sodium silicate (PQ Britesil H20)	30.0
Sodium Percarbonate	9.0
TAED (tetraacetylenediamine)	3.6
Protease (Novo Savinase 6T)	3.0
Amylase (Novo Termamyl 60T)	1.8
Lipase (Novo Lipolase 100T)	0.2
Nonionic (BASF Plurafac LF403)	1.4
Lime soap dispersants were incorporated into the described base at a level of 5% by wt. in addition to the above composition.	

A ten cycle test procedure was used as follows:

Five glass tumblers and two polyethylene plates were placed in a Bosch model 6082 dishwasher along with a bal-  
last load of clean dishware consisting of 9 ceramic dinner plates, 2 ceramic tea cups, 2 stainless steel plates, and 2  
melamine plates. Twenty grams of ASTM standard soil consisting of 80% margarine and 20% powdered milk was  
added to the dishwasher by spreading it onto the inside of the machine door. The 50° C. Economy wash setting was  
used, with water of 300/320 ppm. permanent/temporary hardness expressed as CaCO<sub>3</sub> equivalent (4:1 Ca/Mg ratio).  
18.0 g detergent was added at the start of the main wash, along with lipase (Lipolase 100T ex. Novo) and selected pol-  
ymer (5% by wt. in addition to the detergent composition) as specified. At the end of each complete cycle, fresh soil and  
detergent were added and the process repeated for a total of ten washes.

At the end of this process the tumblers and polyethylene items were visually graded for spotting and filming. Grad-  
ing scales of from 0 to 5 were used to measure film deposition, where a grade of 0 indicates no visible film and a grade  
of 5 indicates coverage with a very heavy, opaque film. When lipase is present in the detergent composition, a film  
buildup can occur on the hydrophobic polyethylene articles, caused primarily by precipitated Ca soap. Thus, film scores  
for the polyethylene articles give an indication of lime soap dispersant efficacy.

For spotting, the number of spots on each item was counted, with the average number of spots per article reported.  
The number of spots on the glass tumblers gives an indication of the effectiveness of the lipase. When lipase is present  
in the detergent composition, the lowest number of spots corresponds to the most effective lipase action.  
The following spotting and filming grades were obtained (as noted, filming on polyethylene items in the presence of  
lipase is primarily caused by lime soap deposition):

Composition	Glass Tumblers		Polyethylene Items	
	mineral film		lime soap	
	film score	# of spots	film score	# of spots
(1) Base formulation	1.0	225	3.0	138
(2) Base + lipase, no dispersant	1.0	1	5.0	0
(3) Base + lipase + amphoteric polymer (PC2)	1.5	0	2.5	0
(4) Base + Lipase + C13-C15 EO12 alcohol ethoxylate	0.5	51	2.0	33
(5) Base + Lipase + C12-C15 EO3 alcohol ethoxysulfate	0.5	120	0.0	127

As this example demonstrates, addition of lipase to the base formulation results in a significant reduction in the  
number of spots on the glass tumblers (Composition 2). This is indicative of lipase functioning in the system. However,  
filming on polyethylene items is very high, due to lime soap deposition. Addition of an amphoteric polymer within the  
scope of the invention (Composition 3) significantly reduces the film score on polyethylene items, while the excellent  
glassware appearance produced by lipase is retained, as seen by the low spotting scores on the glass tumblers. In con-  
trast, while the materials described in WO94/07984 and WO/07985 (incorporated in Compositions 4 and 5) reduce lime  
soap deposition, they also greatly reduce

Example 3

The ability of amphoteric polymers to reduce lime soap deposition without inhibiting the antispotting benefit pro-  
vided by lipase was further demonstrated as follows:

The ten wash cycle test procedure described in example 2 was followed. The base dishwashing detergent compo-  
sition as described in Table 2 was used for this example, but was dosed at 26.0 g instead of the 18.0 g used in example  
2. Amphoteric polymers were added to this composition at a level of 4%, as opposed to the 5% used in the previous  
example. All other test parameters were identical to those for example 1.

The following spotting and filming grades were obtained (as noted, filming on polyethylene items is primarily  
caused by lime soap deposition):

Composition	Glass Tumblers		Polyethylene Items	
	mineral film		lime soap	
	film score	# of spots	film score	# of shots
(1) Base + lipase, no dispersant	2.1	0	1.5	225
(2) Base + lipase + amphoteric polymer (PC2)	2.2	2	0	23
(3) Base + lipase + amphoteric polymer (Alco E-2072)	2.3	2	0.3	30
(4) Base + lipase + amphoteric polymer (Alco E-2075)	1.9	2	0.3	16

This example further illustrates the effectiveness of amphoteric polymers within the scope of the invention in improving glass and plasticware appearance by inhibiting the deposition of lime soap while maintaining the antispotting benefit provided by lipase.

### Claims

1. A method of preventing the deposition of lime soap on tableware in a machine dishwasher comprising the steps of:

a) selecting a detergent composition comprising:

i) an effective amount of an amphoteric polymer wherein in a 1% aqueous solution having a pH of about 7 or greater, positively charged monomers are present on the polymer comprising between 1% and 50% by mole of the polymer, the polymer having a formula selected from the group consisting of:



wherein in a 1% aqueous wash liquor pH A is an anionic moiety, B is a cationic moiety and C is selected from the group consisting of anionic moiety, cationic moiety, amphoteric moiety, uncharged moiety and mixtures thereof, and x is 50-99 mole % and y is 1-50 mole %, and z is 0-25 mole %,

or



wherein in a 1% aqueous wash liquor pH, D is an amphoteric moiety, E is selected from the group consisting of anionic moiety, cationic moiety, uncharged moiety and mixtures thereof, d is 1 to 100 mole %, f is 0-99 mole %;

ii) 0.01% to about 4 wt % of a lipolytic enzyme, and

iii) about 1 to about 75% by wt. of a builder material; and

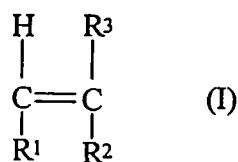
b) applying the detergent composition to soiled tableware to substantially prevent deposition of lime soap on cleaned tableware.

2. A method according to claim 1, wherein x is 80 to about 98 mole %, y is 2-20 mole % and z is 0 to 18 mole %.

3. A method according to claim 1, wherein the anionic moiety A is a substituted vinyl compound.

4. A method according to claim 3, wherein the substituted vinyl compound is a compound of formula I

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wherein  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  each are independently a hydrogen, C1 to C30 alkyl, a carboxylate group or a carboxylate group substituted with a C1 to C30 straight or branched alkyl, aromatic heterocycle or a polyalkylamine oxide provided that at least one of  $\text{R}^1$ ,  $\text{R}^2$ , or  $\text{R}^3$  is a carboxylate or a substituted carboxylate.

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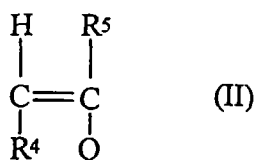
5. A method according to claim 4 wherein the compounds are selected from the group consisting of acrylic acid, methacrylic acid, maleic acid,  $\alpha$ -ethacrylic acid,  $\beta,\beta$ -dimethacrylic acid, methylenemalononic acid, vinylacetic acid, allylacetic acid, ethylideneacetic acid, propylideneacetic acid, crotonic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid and mixtures thereof.

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6. A method according to claim 5 wherein the compounds are selected from the group consisting of acrylic acid, methacrylic acid and maleic acid.

7. A method according to claim 1 wherein the cationic moiety (B) is a substituted vinyl compound of formula II

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wherein  $\text{R}^4$  is a hydrogen, aromatic, heterocycle or a polyalkylamine oxide;  $\text{R}^5$  is a hydrogen or a C1 to C30 straight or branched alkyl; and Q is a nitrogen-containing organic radical, said radical having a pKa value of  $> 7$ .

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8. A method according to claim 7 wherein the compounds of formula II are selected from the group consisting of vinylamine, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylamide and dialkylaminoalkyl acrylamide.

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9. A method according to claim 7 wherein Q is a compound selected from the group consisting of formula III



wherein  $\text{X}^-$  is any suitable counterion such as halogen, hydroxide, sulfate, hydrosulfate, phosphate, formate and acetate;

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or formula IV

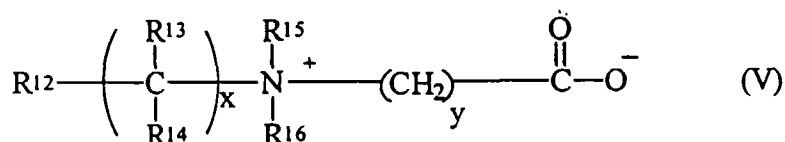


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wherein Z is selected from the group consisting of O, COO and  $\text{CONR}_{11}$  in which  $\text{R}^{11}$  is a hydrogen or a C1 to C3 alkyl group;  $\text{R}^6$  and  $\text{R}^7$  are each independently selected from the group consisting of hydrogen, C1 to C4 alkyl or  $\text{R}^6$  and  $\text{R}^7$  taken together form a C3 to C7 aliphatic heterocycle; m is 0 to 2 provided that when m is 0 a C-N bond is present in lieu of the  $(\text{CH}_2)_m$  group and  $\text{R}^8$ ,  $\text{R}^9$ , and  $\text{R}^{10}$  are each independently selected from a group consisting of hydrogen or a C1 to C4 alkyl; or  $\text{R}^8$  and  $\text{R}^9$  are taken together with the nitrogen to which they are attached to form a 3 to 7 membered non-aromatic nitrogen heterocycle; and X is any suitable counterion such as a halogen, hydroxide, sulfate, hydrosulfate, phosphate, formate and acetate.

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10. A method according to claim 1 wherein the amphoteric moiety (D) has formula



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wherein R<sup>12</sup> is a C<sub>3</sub>-C<sub>6</sub> monoethylenically unsaturated carboxylate;  
 R<sup>13</sup> and R<sup>14</sup> each independently represent hydrogen or a C<sub>1-3</sub> alkyl; R<sup>15</sup> and R<sup>16</sup> each represent a hydrogen or a C<sub>1-3</sub> alkyl, x is 1-3 and y is 1-3.

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11. The method according to claim 10 wherein R<sub>12</sub> is a carboxylate selected from the group consisting of acrylic acid, methacrylic acid, α-ethacrylic acid, β,β-dimethacrylic acid, methylenemalononic acid, vinylacetic acid, allylacetic acid, ethylideneacetic acid, propylideneacetic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, and alkali metal and ammonium salts thereof.

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12. The method according to claim 1 wherein the amphoteric polymer is a copolymer of acrylic acid and 3-acrylamidopropyl trimethylammonium chloride.

13. The method according to claim 1 wherein the amphoteric polymer is a terpolymer of acrylic acid, dimethyldiallylammonium chloride, and C14-20 EO 20 itaconate ester.

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14. The method according to claim 1 wherein the amphoteric polymer is present in an amount of from 0.1 to about 25 wt. %.

15. The method according to claim 1 wherein the detergent composition further comprises a protease, an amylase and mixtures thereof.

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16. A detergent composition useful for preventing deposition of lime soap on tableware in a machine dishwasher comprising:

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i) an effective amount of an amphoteric polymer wherein in a 1% aqueous solution having a pH of about 7 or greater, positively charged monomers are present on the polymer comprising between 1% and 50% by mole of the polymer, the polymer having a formula selected from the group consisting of:



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wherein in a 1% aqueous wash liquor pH A is an anionic moiety, B is a cationic moiety and C is selected from the group consisting of anionic moiety, cationic moiety, amphoteric moiety, uncharged moiety and mixtures thereof, and x is 50-99 mole % and y is 1-50 mole %, and z is 0-25 mole %, and

or

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wherein in a 1% aqueous wash liquor pH, D is an amphoteric moiety, E is selected from the group consisting of anionic moiety, cationic moiety, uncharged moiety and mixtures thereof, d is 1 to 100 mole %, f is 0-99 mole %;

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ii) 0.01% to about 4 wt % of a lipolytic enzyme; and

iii) about 1 to about 75% by wt. of a builder material.

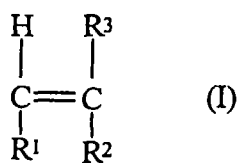
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17. A composition according to claim 16 wherein x is 80 to about 98 mole %, y is 2-20 mole % and z is 0 to 18 mole %.

18. A composition according to claim 16 wherein the anionic moiety A is a substituted vinyl compound.

19. A composition according to claim 18 wherein the substituted vinyl compound is a compound of formula I

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wherein R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> each are independently a hydrogen, C1 to C3 alkyl, a carboxylate group or a carboxylate group substituted with a C1 to C30 straight or branched alkyl, aromatic heterocycle or a polyalkylamine oxide provided that at least one of R<sup>1</sup>, R<sup>2</sup>, or R<sup>3</sup> is a carboxylate or a substituted carboxylate;

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20. A composition according to claim 19 wherein the compounds are selected from the group consisting of acrylic acid, methacrylic acid, maleic acid,  $\alpha$ -ethacrylic acid,  $\beta,\beta$ -dimethacrylic acid, methylenemalonic acid, vinylacetic acid, allylacetic acid, ethylideneacetic acid, propylideneacetic acid, crotonic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid and mixtures thereof.

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