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Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 554 943 A2

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **93200217.3**(51) Int. Cl.⁵: **C11D 3/00, C11D 3/08,
C11D 1/83**(22) Date of filing: **28.01.93**

A request for correction of the description and of claim 4 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, 2.2).

(30) Priority: **03.02.92 GB 9202237
17.03.92 EP 92302290**(43) Date of publication of application:
11.08.93 Bulletin 93/32(84) Designated Contracting States:
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(54) **Detergent composition.**

(57) A chlorine bleach-free aqueous liquid machine dishwashing composition having solution pH 7-11 contains proteolytic enzyme, detergency builder, sodium silicate having SiO₂:Na₂O ratio of from 2.0-3.2 and organic surfactant which comprises (i) glycoside surfactant, (ii) anionic sulphate or sulphonate including a C₈ to C₂₂ alkyl or alkenyl group or (iii) ethoxylated C₆ to C₁₆ fatty alcohol with HLB of at least 10.5, or a mixture of (i), (ii) and/or (iii). If (iii) is used without (ii) it must be an ethoxylated C₆ to C₁₂ alcohol, or glycoside surfactant must also be present. Proteolytic enzyme plus the specified surfactant gives a synergistic improvement in removal of proteinaceous soil.

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Field of the Invention

The present invention relates to an aqueous liquid detergent product particularly adapted for use in a machine dishwasher.

Background and Prior Art

Liquid automatic dishwasher detergent compositions, both aqueous and non-aqueous, have recently received much attention and the aqueous products have achieved commercial popularity.

The acceptance and popularity of the liquid formulations as compared to the more conventional powdered products stems from the convenience and performance of the liquid products. However the currently available and proposed liquid product formulations are based on the concept of the conventional machine dishwashing powder compositions which are highly alkaline and highly built products containing a chlorine bleach (see for example EP-A-0,517,308 and EP-A-517,309).

It has now surprisingly been found that a mild and yet quite effective aqueous liquid machine dishwashing detergent composition can be formulated based on certain surfactants and proteolytic enzymes wherein there is an apparent synergistic effect between the active and the protease enzyme, especially in the removal of protein soil.

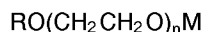
The use of glycosides in detergent compositions has been disclosed in a number of documents. WO 86/05187 (Staley) discloses laundry detergent compositions comprising glycoside surfactant and enzyme. Various enzymes are mentioned.

DE 38 33 047 discloses acidic powdered dishwashing compositions containing alkyl glycoside in combination with other surfactant and amylase. These compositions are acidic and have solution pH below 6.

Summary of the Invention

According to the invention there is provided a chlorine bleach-free aqueous liquid machine dishwashing detergent composition comprising :

- (a) from 0.0002 to 0.05 Anson units per gram of the composition of a proteolytic enzyme;
- (b) from 5 to 90% by weight of a detergency builder;
- (c) from 1 to 40% by weight of sodium or potassium silicate having $\text{SiO}_2:\text{Na}_2\text{O}$ or $\text{SiO}_2:\text{K}_2\text{O}$ ratio of from about 2.0 to about 3.2.
- (d) from 3 to 50% by weight of an organic surfactant selected from the group of:
 - (i) glycoside surfactants;
 - (ii) anionic surfactants with a hydrophilic head group which is, or which contains a sulphate or sulphonate group and a hydrophobic portion which is or which contains an alkyl or alkenyl group of 8 to 22 carbon atoms;
 - (iii) ethoxylated fatty alcohols of formula



where R is an alkyl group of 6 to 16 carbon atoms and n has an average value which is at least four and is sufficiently high that the HLB value of the ethoxylated fatty alcohol is 10.5 or greater, with the proviso that if ethoxylated fatty alcohol (iii) is used without anionic surfactant (ii) the majority of its alkyl groups R contain 6 to 12 carbon atoms; and

(iv) mixtures thereof;

(e) water, said composition having a pH of 7 to 11, if added deionised water at a concentration of 2 g/l.

In a second aspect this invention provides a method of washing crockery and/or glassware comprising exposing the crockery and/or glassware to a mixture of water and a detergent composition as specified above. In another aspect the invention provides use of such a composition in machine dishwashing.

Detailed DescriptionThe Proteolytic Enzyme

Protease can, for example, be used in an amount ranging from about the order of 0.0002 to about the order of 0.05 Anson units per gram of the detergent composition, preferably 0.001 to 0.025 Anson units.

Expressed in other units, the protease can also be included in the compositions in amounts of the order of from about 0.5 to 100 GU/mg of the detergent composition. Preferably, the amount ranges from 1 to 50, and particularly preferably from 2 or even 5 to 15 or 20 GU/mg of composition.

A GU is a Glycine Unit, defined as the proteolytic enzyme activity which, under standard conditions, during a 15-minute incubation at 40 °C with N-acetyl casein as substrate, produces an amount of NH₂-group equivalent to 1 micromole of glycine.

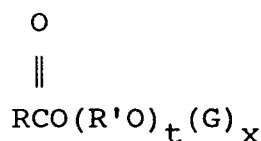
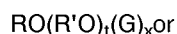
Enzyme activities are sometimes also measured in kilo Novo units (KNPU): a measurement depending on the type of protease and assay used. We have found that the KNPU/AU ratio is in the range of about 3:1 to 5:1 for Alcalase, Esperase and Savinase and for the purpose of these formulations it is not necessary to be more precise.

Preferred examples of protease enzyme to be used in the present compositions are the subtilisin varieties sold as Savinase (TM of Novo-Nordisk A/S) or Maxacal (TM of Gist-Brocades/IBIS) or as Opticlean (ex MKC) or AP122 (ex Showa Denko), which has pI approximately 10. Other useful examples of proteases include Maxatase, Esperase, Alcalase (Trade Marks), protinase K and subtilisin BPN'. Protinase K can also be used.

Organic surfactant

Glycoside Surfactant

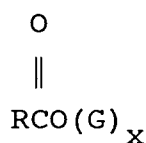
This will be nonionic in character and of course includes glycoside residues. Suitably it is of the general formula :



in which G is a residue of a pentose or hexose, R'O is an alkoxy group, x is at least unity and R is an organic hydrophobic group which is preferably aliphatic, either saturated or unsaturated, notably straight or branched alkyl, alkenyl, hydroxyalkyl or hydroxyalkenyl. However, it may include an aryl group, for example alkyl-aryl, alkenyl-aryl and hydroxyalkyl-aryl. It is envisaged that R may be from 6 to 20 carbon atoms.

Particularly preferred is that R is alkyl or alkenyl of 7 to 14 or 16 carbon atoms, especially 7 to 12.

The value of t in the general formula above is preferably zero, so that the -(R'O)_t- unit of the general formula is absent. In that case the general formula becomes :



If t is non-zero, it is preferred that R'O is an ethylene oxide residue. Other possibilities are propylene oxide and glycerol residues. If the parameter t is non-zero so that R'O is present, the value of t (which may be an average value) will preferably lie in the range from 0.5 to 10.

The group G is typically derived from fructose, glucose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose and/or ribose. Preferably, the G is provided substantially exclusively by glucose units. Intersaccharide bonds may be from a 1-position to a 2, 3, 4 or 6-position of the adjoining saccharide. Hydroxyl groups on sugar residues may be substituted, e.g. etherified with short alkyl chains of 1 to 4 carbon atoms. Preferably a sugar residue bears no more than one such substituent.

The value x, which is an average, is usually termed the degree of polymerization. Desirably x varies between 1 and 8. Values of x may lie between 1 and 3, especially 1 and 1.8.

Alkyl polyglycosides of formula $RO(G)_x$, i.e. a formula as given above in which t is zero, are available from BASF and Henkel.

Alkyl polyglycosides of particular interest have x in the narrow range from 1 or 1.2 up to 1.4 or especially 1.3. If x exceeds 1.3, it preferably lies in the range from 1.3 or 1.4 to 1.8.

When x lies in the range from 1 to 1.4, it is preferred that R is C_8 to C_{14} alkyl or alkenyl.

O-alkanoyl glucosides are described in International Patent Application WO 88/10147 (Novo Industri A/S). In particular the surfactants described therein are glucose esters with the acyl group attached in the 3- or 6-position such as 3-O-acyl-D-glucose or 6-O-acyl-D-glucose. Notable are 6-O-alkanoyl glucosides, in which the alkanoyl group incorporates an alkyl or alkenyl group having from 7 to 13 preferably 7, 9 or 11 carbon atoms. The glucose residue may be alkylated in its 1-position with an alkyl group having from 1 to 4 carbon atoms, such as ethyl or isopropyl. Alkylation in the 1-position enables such compounds to be prepared by regiospecific enzymatic synthesis as described by Bjorkling et al. (J. Chem. Soc., Chem. Commun. 1989 p934).

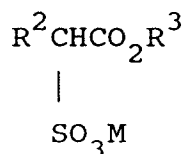
While esters of glucose are contemplated especially, it is envisaged that corresponding materials based on other reducing sugars, such as galactose and mannose are also suitable.

Anionic surfactant

Preferred anionic surfactants are one or a mixture of:
primary alkyl sulphate of formula:



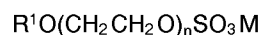
where R^1 is a primary alkyl group of 8 to 18 carbon atoms and M is a solubilising cation,
fatty acid ester sulphonate of formula



where R^2 is an alkyl group of 6 to 16 carbon atoms, R^3 is an alkyl group of 1 to 4 carbon atoms and M is a solubilising cation,
alkyl benzene sulphonate of formula



where R^4 is an alkyl group of 10 to 16 carbon atoms and M is a solubilising cation,
alkyl ether sulphate of formula



where R^1 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 solubilising cation.

Especially preferred as surfactant is primary alkyl sulphate. In its general formula

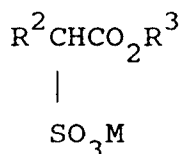


the solubilising cation may be a range of cations which are general monovalent and confer water solubility. Alkali metal, notably sodium, is especially envisaged. Other possibilities are ammonium and substituted ammonium, such as trialkanolammonium.

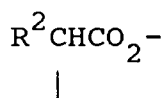
The alkyl group R¹ may have a mixture of chain lengths. It is preferred that at least two thirds of the R¹ alkyl groups have a chain length of 8 to 14 carbon atoms. This will be the case if R¹ is coconut alkyl, for example.

If the surfactant is fatty acid ester sulphonate, alkyl benzene sulphonate or alkyl ether sulphonate the solubilising cation M may be a range of cations as discussed above for alkyl sulphate.

In the general formula for fatty acid ester sulphonate:



the group R² 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:



is derived from a coconut source, for instance.

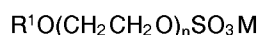
The group R³ may be any C₁ to C₄ alkyl group. Straight chain alkyl may be preferred, notably methyl or ethyl.

In the general formula formula of alkyl benzene sulphonate:



The group R⁴ may be a mixture of chain lengths. Preferred are straight chains of 11 to 14 carbon atoms.

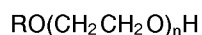
In the general formula for alkyl ether sulphate:



the group R¹ is as discussed for alkyl sulphate. Preferably n has an average value of 2 to 5.

Nonionic surfactant

Ethoxylated fatty alcohol may be used alone or in admixture with anionic surfactants, especially the preferred surfactants above. However, if it is used alone than the fatty alcohol must be of limited chain length so that average chain lengths of the alkyl group R in the general formula:



is from 6 to 12 carbon atoms. This is preferred in any event, and especially preferred if the weight of anionic surfactant is less than half the weight of ethoxylated fatty alcohol.

Notably the group R may have chain lengths in a range from 9 to 11 carbon atoms.

An ethoxylated fatty alcohol normally is a mixture of molecules with different numbers of ethylene oxide residues. Their average number, n, together with the alkyl chain length, determines whether the ethoxylated fatty alcohol has a hydrophobic character (low HLB value) or a hydrophilic character (high HLB value). For this invention the HLB value should be 10.5 or greater. This requires the average value of n to be at least 4, and possibly higher. 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 which has 9 to 11 carbon atoms while n is from 5 to 8.

Other surfactant

The above surfactant, or a mixture of two or more of them, may possibly be accompanied by some other detergent active, usually in a lesser quantity. Preferably the amount of any other detergent surfactant will be no more than one third of the total weight of detergent surfactant present, or even no more than one quarter.

If other surfactant is included it may be anionic or nonionic in character, or possibly amphoteric or zwitterionic. Cationic surfactant is possible if anionic is absent, but is not preferred. Soap may optionally be included, as well as non-soap surfactants.

One significant possibility is the use of a surfactant or mixture of surfactants of the above specified anionic and/or nonionic types, together with glycoside surfactants of the above specified type.

As mentioned, the amount of glycoside surfactant, anionic surfactant and/or ethoxylated fatty alcohol surfactant will be from 3 to 50% by weight of the composition. Desirably the total amount of surfactant lies in the same range. Preferred ranges, both for the specified surfactant and total surfactant are 3 to 30% by weight, more preferably, in the range from 5 or 10% to 25% by weight.

Detergent Builder Materials

The cleaning compositions of this invention can contain all manner of detergent builders commonly taught for use in automatic dishwashing or other cleaning compositions. The builders can include any of the conventional inorganic and organic water-soluble builder salts, also insoluble inorganic builders or mixtures thereof, and may comprise from 5 to 90% by weight of the detergent composition.

Typical of the well-known inorganic builders are the sodium and potassium salts of the following: pyrophosphate, tripolyphosphate, orthophosphate, carbonate, bicarbonate, sesquicarbonate and borate. Other non-phosphorous salts including (insoluble) crystalline and amorphous aluminosilicates (e.g. zeolites) may be used as well.

Preferred builders can be selected from the group consisting of sodium tripolyphosphate, sodium carbonate, sodium bicarbonate and mixtures thereof. When present in these compositions, sodium tripolyphosphate concentrations will usually range from 2% to 40%, preferably from 5% to 30%. Sodium carbonate and bicarbonate, when present, can range from 10% to 50%, preferably from 20% to 40% by weight of the cleaning compositions. Potassium pyrophosphate is a preferred builder in gel formulations, where it may be used at from 3 to 30%, preferably from 10 to 20%.

Organic detergent builders can also be used in the present invention. They are generally sodium and potassium salts of the following: citrate, malonate or succinate substituted with a C_8 to C_{24} alkyl group, nitrilotriacetates, phytates, polyphosphonates, oxydisuccinates, oxydiacetates, carboxymethyloxy succinates, tetracarboxylates, starch, oxidized heteropolymeric polysaccharides, and polymeric polycarboxylates such as polyacrylates of molecular weight of from about 5,000 to about 200,000. Polyacetal carboxylates such as those described in U.S. Patent Nos. 4,144,226 and 4,146,495 may also be used.

Non-phosphate builders are particularly preferred for environmental reasons.

Sodium citrate is an especially preferred builder. When present, it is preferably used in an amount from about 1% to about 75% of the total weight of the detergent composition, especially 10 to 50% by weight.

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

Silicate

The compositions of this invention contain sodium or potassium silicate at a level of from about 1 to about 40% by weight of the cleaning composition, more preferably from 5 to 25%, even more preferably from 7 to 20%. This material is employed as a cleaning ingredient, source of alkalinity, metal corrosion inhibitor and protector of glaze on china tableware. The sodium or potassium silicate usable herein will have a ratio of $SiO_2:Na_2O$ or $SiO_2:K_2O$ of from about 2.0 to about 3.2. Some of the silicate may be in solid form. Useful is sodium silicate having a ratio of $SiO_2 : Na_2O$ of higher than 2.0, preferably at least 2.4.

If a composition contains less than 10% silicate, we prefer to include a zinc salt, such as zinc sulphate, especially if the composition dissolves to give an alkaline pH, e.g. pH over 8.5. Such a zinc salt serves to protect glassware from attack by an alkaline wash liquor, and may suitably be used in amounts from 0.1 to

3% by weight.

Other Optional Ingredients

5 Bleach system

Compositions according to the present invention are free from chlorine bleach compounds but may contain a peroxygen bleach component. If present the amount will preferably lie in a range from 1 to 30% by weight.

10 A peroxygen bleach which may be employed is for example sodium perborate. This is preferably accompanied by a bleach activator which allows the liberation of active oxygen species at a lower temperature. A preferred bleach activator is tetraacetyl ethylene diamine (TAED) but other activators for perborate are known and can be used. The amounts of peroxygen bleach and bleach activator in an individual composition preferably do not exceed 20% and 15% by weight respectively.

15 Another peroxygen bleach is sodium percarbonate. Yet another is sodium monopersulphate. Further peroxygen bleaches which may be used are alkyl, alkenyl and aryl peroxy organic acids and their metal salts. Typical peroxy acids include

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- α -naphthoic acid
- (ii) aliphatic and substituted aliphatic monoperoxy acids, e.g. peroxy lauric acid and peroxy stearic acid
- 20 (iii) 1,12-diperoxydodecanedioic acid (DPDA)
- (iv) 1,9-diperoxyazelaic acid
- (v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid
- (vi) 2-decyldiperoxybutane-1,4-dioic acid.
- (vii) phthaloylamidoperoxy caproic acid (PAP).

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Thickeners and 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. Use of clay thickeners for automatic dishwashing compositions is disclosed, for example, in U.S. Patents Nos. 4,431,559; 4,511,487; 4,740,327; 4,752,409. Use of salts of polymeric carboxylic acids is disclosed, for example, in UK Patent Application GB 2,164,350A. 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.

Various polymers may be included. These may in particular assist in detergency building or be polymeric thickeners, which may be used alone or jointly with other types of thickeners. Notable are polymers containing carboxylic or sulphonic acid groups in acid form or wholly or partially neutralised to sodium or potassium salts, the sodium salts being preferred. Preferred polymers are homopolymers and copolymers of acrylic acid and/or maleic acid or maleic anhydride. Of especial interest are polyacrylates, polyalphanhydroxy acrylates, acrylic/maleic acid copolymers, and acrylic phosphinates. Other polymers which are especially preferred for use in liquid detergent compositions are deflocculating polymers such as for example disclosed in EP 346995.

45 The molecular weights of homopolymers and copolymers are generally 1000 to 150,000, preferably 1500 to 100,000. Polyacrylate thickeners may well have molecular weights from 300,000 up to 6 million. The amount of any polymer may lie in the range from 0.5 to 5% or even 10% by weight of the composition.

For liquid formulations with a "gel" appearance and rheology, particularly if a clear gel is desired, a chlorine-stable polymeric thickener is particularly useful. U.S. Patent No. 4,260,528 discloses natural gums and resins for use in clear autodish detergents, which are not chlorine-stable. Crosslinked acrylic acid polymers manufactured by B.F. Goodrich and sold under the trade name "Carbopol" have been found to be effective for production of clear gels, and Carbopol 940 having a molecular weight of about 4,000,000 is particularly preferred for maintaining high viscosity with excellent chlorine stability over extended periods. Further suitable chlorine-stable polymeric thickeners are described in U.S. Patent 4,867,896.

55 The amount of thickener employed in the composition, including any polymeric thickener, may range from 0 to 5%, preferably 1 to 3%.

Stabilizers and/or co-structurants such as long-chain calcium and sodium soaps and C₁₂ to C₁₈ alkyl sulphates are detailed in U.S. Patents Nos. 3,956,158 and 4,271,030 and the use of other metal salts of

long-chain soaps is detailed in U.S. Patent No. 4,752,409. 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 0.1-2%. 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 composition and/or water-soluble structuring chelants at 1-60%. These co-structurants are more fully described in EP-A-323209.

Defoamer

A significant consideration, in machine dishwashing compositions, is the need to suppress foaming. The agitation conditions in a dishwashing machine are more rigorous than those in a fabric washing machine and lead to foam formation. Some food residues, such as egg and cream, also lead to the generation of foam.

Foam, if it forms, can cause air to be drawn into the circulating pump. This can interfere with proper water circulation and the supply of water to the heating element. Excessive foam generation can eventually lead to air locking of the pump, which could wreck the machine by stopping the water supply to the heating element.

A composition of the invention may further include defoamer. Even if the cleaning composition has only low foaming surfactant, presence of a defoamer can assist to minimize foam which food soils can generate.

Current machine dishwashing compositions contain a nonionic surfactant which includes ethylene oxide and propylene oxide residues. These surfactants have cloud points below the operating temperature and they therefore form hydrophobic droplets which exert an antifoam action.

Materials which may be utilised as defoamer in a composition of this invention include mono- and di- C_8 to C_{22} alkyl phosphates and mineral oil/or wax. These may be used as a combination containing particles of the insoluble alkyl phosphate together with petroleum jelly. Possible alternatives to the alkyl phosphate include ethylene distearamide, calcium soap and finely divided silica, especially hydrophobed silica. Mineral oils and waxes which may be used include petroleum fractions, Fischer-Tropsch waxes, ozokerite, ceresin montan wax, beeswax, candelilla wax, camauba wax and mixtures thereof.

A further category of materials which may be used are ketones of formula R^7COR^8 wherein R^7 and R^8 are both alkyl or alkenyl groups containing 8 to 24 carbon atoms and such that the ketone contains 25 to 49 carbon atoms. Ketones of this type and their use as antifoam agents in (other) machine dishwashing compositions, are disclosed in EP-A-324339.

Another category of material which can be used as a defoamer is soap or fatty acid which becomes neutralised to soap in use of the composition. Such soap or fatty acid should have an acyl group of 12 to 22 carbon atoms, especially 14 to 18 carbon atoms. If soap or fatty acid is used as defoamer some calcium salt may deliberately be included in the composition, thereby ensuring the presence of calcium ions to form a calcium soap which exerts the antifoaming action.

If present, the composition may include 0.1 to 30% by weight of defoamer, preferably other than nonionic surfactant. Non-soap defoamer may be used at levels towards the lower end of this range, e.g. 0.1 to 10%, preferably 0.5 to 2% or 5%. Soap or fatty acid can be used as defoamer, and if present may be used in amounts from 0.1 to 30% by weight, especially 0.5 to 10%.

If the surfactant is alkyl sulphate alone, it may be desirable to use a said ketone (in branched chain alcohol), soap or fatty acid as the defoamer and to avoid alkyl phosphates or mineral oil.

Minor amounts of various other components may be present in the cleaning composition. These include anti-scalants, corrosion-inhibitors anti-redeposition agents, anti-tarnish agents, other enzymes (especially amylase and/or lipase at 0.05-2% by weight, preferably 0.5-1.5%) and other functional additives and perfume.

As revealed above the compositions of this invention may take the form of a liquid or a gel.

The composition is preferably formulated to give a pH in the range 7 to 11, even better 8 to 11 if added to deionized water at a concentration of 2.0 grams/litre. A particularly preferred pH is 9.0 to 9.5.

The following examples will more fully illustrate the embodiments of the invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

Example 1

This example demonstrates action of removing soil from glass slides.

New glass slides, 5cm x 5cm were machine washed, repeatedly rinsed with demineralised water and soiled with about 55mg baked on egg-yolk per slide.

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All washing solutions contained, in 1 litre of 16° French hardness water:

Sodium citrate dihydrate	0.445g
Acrylic-maleic copolymer (Sokolan CP5)	0.111g
Sodium disilicate monohydrate*	0.445g
Potassium coconut soap	0.100g
Sodium sulphate dihydrate	0.950g
Calcium sulphate	0.03g

* $\text{SiO}_2:\text{Na}_2\text{O} > 2.0$

These materials were added to the water and stirred at 45°C for 15 minutes. Some solutions then received:-

30mg Savinase 6.0CM (sold as having 1500 GU/mg, analysed as 1544 GU/mg) and/or 0.5g alkyl polyglycoside of formula $\text{RO}(\text{G})_x$ where $\text{R} = \text{C}_{12}\text{-C}_{14}$ alkyl, G denotes a glucose residue and x has an average value of 1.3.

The solutions were maintained at 45°C.

After one minute slides were placed in the solution. Slides were removed after varying periods of time, dried and weighed to determine stain removal. The quantity removed was expressed as a percentage of the original stain.

Results were as follows:-

% Egg-yolk removal				
Wash Time (minutes)	No enzyme No APG	Enzyme only	APG only	APG + Enzyme
1	1.7	1.5	0.8	1.2
5	1.5	2.0	0.9	1.7
10	1.9	3.1	0.4	4.4
20	2.0	4.4	-0.2	15.2
30	2.4	5.8	0.2	22.4
40	2.6	8.1	-0.6	31.3
50	2.5	12.8	-1.1	48.1
60	2.6	20.1	-1.4	70.6

These results show synergistic enhancement of stain removal through the use of APG jointly with the proteolytic enzyme, with washing periods of 10 minutes or longer.

Example 2

The procedure was similar to Example 1. All solutions contained, per litre of water:-

Sodium citrate dihydrate	0.60g
Acrylic maleic copolymer	0.15g
Sodium disilicate monohydrate	0.60g

Some solutions received 0.5g of alkyl polyglycoside and/or 30mg of Savinase (both as used in Example 1). Further solutions received 0.5g of C_{13} to C_{15} alcohol 3EO (Synperonic A3) and/or 30mg Savinase. Slides were maintained in the solution at 45°C for 60 minutes.

Results were:-

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Solution contained	wt% egg-yolk removal
Savinase only	24.3 ± 4.5
APG only	0.7 ± 0.6
Synperonic A3 only	3.0 ± 1.1
APG + Savinase	53.0 ± 8.0
Synp.A3 + Savinase	26.3 ± 14.5

Clearly synergy with APG exceeded synergy (if any) with Synperonic A3.

Example 3

The procedure was the same as in Example 2. All solutions contained in 1 litre water:-

Sodium tripolyphosphate	1.16g
Sodium carbonate	0.27g
Sodium disilicate hydrate	0.32g

Some solutions received 0.5g of alkyl polyglycoside and/or 30mg of Savinase (both as used in Example 1). Further solutions received 0.5g of C₁₃ to C₁₅ alcohol 3EO (Synperonic A3) and/or 30mg Savinase. Slides were maintained in the solution at 45 ° C for 60 minutes.

Results were:-

Solution contained	Egg-yolk removal (wt%)
Savinase	15.8 ± 6.3
APG	3.6 ± 1.6
Synperonic A3	5.3 ± 2.0
APG + Savinase	42.5 ± 15.1
A3 + Savinase	14.4 ± 1.6

Again, APG plus Savinase gave the best soil removal.

Example 4

The procedure was similar to Example 1. Several types of alkyl polyglycoside were employed. All solutions contained, per litre of water:-

Sodium citrate dihydrate	0.60g
Acrylic maleic copolymer	0.15g
Sodium disilicate monohydrate	0.60g
Alcalase 2.0T	30mg (giving activity 46 GU/ml of solution).

All solutions received 0.5g of alkyl polyglycoside of general formula RO(G)_x where G denotes a glucose residue and R is an alkyl chain. The alkyl polyglycoside displayed various alkyl chain lengths R and various values of x, the degree of polymerisation.

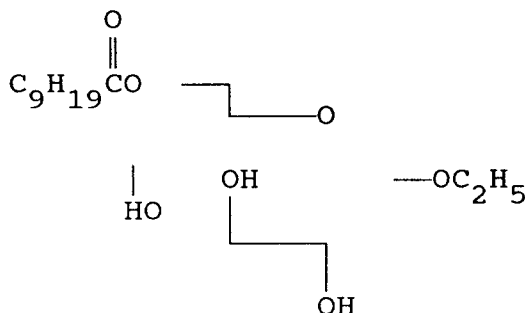
Slides were maintained in the solutions at 45 ° C for 40 minutes. The alkyl polyglycoside characteristics and the results obtained were:-

No of carbon atoms in alkyl chain R	Degree of polymerisation	wt% egg-yolk removal
9-11	1.4	86.6 ± 4.6
9-11	1.8	79.7 ± 9.2
12-13	1.8	54.1 ± 4.6
14	1.4	43.3 ± 5.4
12-14 *	1.3 *	58.0 ± 5.2
10-12	1.3	86.0 ± 4.5

* Same as used in Examples 1 to 3.

Example 5

Again the procedure was similar to Example 1. The detergent active used was ethyl 6-O-decanoyl glucoside which has the formula



All solutions contained, per litre of water:-

Sodium citrate dihydrate	0.60g
Acrylic maleic copolymer	0.15g
Sodium disilicate monohydrate	0.60g

Some solutions also contained:-

30mg Alcalase 2.OT (giving an activity of 46 GU/ml) and/or 0.5g ethyl 6-O-decanoyl glucoside

The solutions were used to wash glass slides stained with egg-yolk as in Example 1, or stainless steel slides stained with egg-yolk in the same way.

Slides were maintained in the solutions at 45 °C, removed after varying periods of time, dried and weighed to assess stain removal, as in Example 1.

Results were as follows:-

% Egg yolk removal from glass			
Wash time (minutes)	enzyme only	Glucoside only	Enzyme + glucoside
10	4 ± 1	2 ± 1	4 ± 1
20	9 ± 0	0 ± 1	17 ± 8
30	15 ± 1	1 ± 1	34 ± 11
40	27 ± 3	1 ± 1	53 ± 17

% Egg yolk removal from stainless steel			
Wash time (minutes)	enzyme only	Glucoside only	Enzyme + glucoside
10	4 ± 0	2 ± 0	4 ± 0
20	8 ± 1	2 ± 0	9 ± 8
30	16 ± 1	2 ± 1	34 ± 7
40	25 ± 4	2 ± 0	54 ± 11

The use of enzyme and glucoside together is thus seen to give a synergistic enhancement of stain removal.

Example 6

A machine dishwashing formulation was a mixture containing:

	Amount by weight	Percent by weight
Na-citrate dihydrate	2.67g	18.5%
Acrylic-maleic copolymer (Sokolan CP5)	0.67g	4.6%
Na-disilicate monohydrate	2.67g	18.5%
Oleic acid	3.44g	23.8%
Ca-stearate	0.30g	2.1%
Petroleum jelly	1.20g	8.3%
APG	3.00g	20.7%
Savinase 6.0CM (1544 GU/mg)	0.30g	2.1%
Termamyl 6OT (4.8MU/mg)	0.20g	1.4%

The alkyl polyglycoside was of the formula $RO(G)_x$ where G denotes glucose, R is a C_{12} - C_{14} alkyl chain and x averages 1.8. This formulation was used to wash various stained glass slides using a Bosch S510 automatic dishwasher on its standard program and without salt added to the machine. The main wash temperature was 55 °C, the final rinse temperature was 65 °C. The water used tap water of 16° French Hardness.

The glass slides were stained with potato, a custard pudding or egg yolk. The potato and custard pudding stains were aged at 30 °C and 60% relative humidity for 16-24 hours. The egg yolk stain was baked-on at 120 °C for two hours. Removal of the stain was determined as loss in weight.

The extent of stain removal was:

Potato	99.7
Custard pudding	92.1
Egg yolk	54.0

Example 7

This example demonstrates synergistic action in removing soil from glass slides.

New glass slides, 5cm x 5cm were machine washed, repeatedly rinsed with demineralised water and soiled with about 55mg baked on egg-yolk per slide.

All washing solutions contained, in 1 litre of 16° French hardness water:-

Sodium citrate dihydrate	0.6 g
Acrylic-maleic copolymer (Sokolan CP5)	0.15 g
Sodium disilicate monohydrate	0.6 g

These materials were added to the water and stirred at 45 °C for 15 minutes. The solutions then received:-

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20mg Alcalase 2.0T (providing 30GU/ml in solution) and/or 0.25g sodium dodecyl sulphate (SDS).

The solutions were maintained at 45 °C.

After one minute slides were placed in the solution. Slides were removed after varying periods of time, dried and weighed to determine stain removal. The quantity removed was expressed as a percentage of the original stain. In this Example only, when a slide was removed from the washing solution it was replaced with a similarly soiled slide which had received identical treatment in a second, identical wash solution.

Results were as follows:-

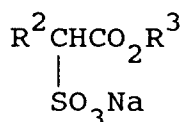
wt% Egg-yolk removal			
Wash Time (minutes)	Enzyme only %	SDS only %	SDS + Enzyme %
10	1.3	-1.1	0.0
20	2.3	-1.0	6.5
30	2.1	-1.2	13.5
40	3.0	-3.3	23.8

These results show synergistic enhancement of stain removal through the use of SDS jointly with the proteolytic enzyme, with washing periods of 20 minutes or longer.

Example 8

Example 7 was repeated, using a larger amount of enzyme and a larger amount of a different anionic surfactant. When slides were removed from the wash solution they were replaced with a clean slide. In consequence the washing solutions received:

30mg Alcalase 2.0T (providing 45 GU/ml in solution) and/or 0.5g of Texin ES68 which is a fatty acid ester sulphonate of formula



in which R² is derived from tallow and so is predominantly C₁₆ and C₁₈ alkyl and R³ is methyl.

The results were:

wt% Egg-yolk removal			
Wash Time (minutes)	Enzyme only	FAES only	FAES + Enzyme
10	6	4	16
20	10	13	44
30	19	16	68
40	26	21	81

The synergistic improvement when using FAES and enzyme together is apparent.

When this experiment was repeated using stainless steel slides the results were almost identical.

Example 9

The procedure of Example 7 was repeated using SDS, and mixtures of SDS with equal weights of other surfactants. For each test the same total amount of surfactant (250mg/l) was used, and 20mg/l of Alcalase 2.0T was present.

The results, expressed as wt% egg-yolk removal after 30 minutes were:

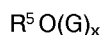
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Surfactant	wt% egg-yolk removal
SDS	66 ± 13
SDS + Dobanol 91-6	69 ± 11
SDS + Synperonic A7	53 ± 9
SDS + APG 300	59 ± 15

Dobanol 91-6 is an ethoxylated fatty alcohol where the fatty alcohol has chain length 9 to 11 carbon atoms and the average degree of ethoxylation is 6. It has an HLB value of 12.5

Synperonic A7 is an ethoxylated fatty alcohol where the fatty alcohol has chain length 13 to 15 carbon atoms and the average number of ethylene oxide residues is 7. It has an HLB value of 12.2.

APG 300 is an alkyl polyglycoside of formula



where R^5 is alkyl of 9 to 11 carbon atoms and x has average value of 1.4.

Example 10

Example 7 was repeated using each of three nonionic surfactants in place of SDS. The results, expressed as wt% egg-yolk removal after 30 minutes, were:

	wt% egg-yolk removal
Synperonic A3 + enzyme	15 ± 3
Synperonic A7 + enzyme	33 ± 6
Dobanol 91-6 + enzyme	53 ± 10

Synperonic A3 is C_{13} - C_{15} fatty alcohol ethoxylated with an average of 3 ethylene oxide residues. It has HLB value 7.9.

Synperonic A7 is, as mentioned in the last example, C_{13} - C_{15} alcohol with an average of 7 ethylene oxide residues. HLB value is 12.2.

Dobanol 91-6 is a C_9 - C_{11} alcohol with an average of 6 ethylene oxide residues. HLB value is 12.5.

It can be seen that this nonionic, used alone, was much superior to Synperonic A7, used alone.

Example 11

Example 7 was repeated twice using a larger amount of enzyme (as in Example 8) and two ethoxylated nonionic surfactants. In consequence the washing solutions received:

30mg Alcalase 2.OT (providing 45 GU/ml in solution) and/or 0.4g of either Synperonic A7 or Dobanol 91-6.

Results, expressed as wt% egg-yolk removal after 30 minutes, were:

wt% egg-yolk removal		
	Synperonic A7	Dobanol 91-6
enzyme only	18.9 ± 6.0	17.1 ± 4.1
surfactant only	8.4 ± 2.7	7.4 ± 5.2
surfactant + enzyme	46.5 ± 7.3	70.5 ± 7.5

This confirms the greater synergy with Dobanol 91-6.

Example 12

Example 7 was repeated using a larger amount of enzyme (as in Examples 8 and 11) and two anionic surfactants. In consequence the washing solutions received:

30mg Alcalase 2.OT (providing 45 GU/ml in solution) and/or 250mg of either Empicol LX or 250 mg/litre of

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either sodium lauryl ether sulphate (LES) with average 3 ethylene oxide residues, or middle cut coconut alkyl sulphate (Empicol LX).

Results, expressed as wt% egg-yolk removal after 30 minutes, were:

	wt% egg-yolk removal
enzyme only	3.7 ± 0.4
Empicol LX only	-2.0 ± 0.2
Empicol LX + enzyme	35.2 ± 2.5
LES only	0.1 ± 0.7
LES + enzyme	31.2 ± 2.6

Example 13

Several machine dishwashing formulations were prepared. Each was a mixture containing:

	Amount by weight
Na-citrate dihydrate	3.0g
Acrylic-maleic copolymer (Sokolan CP5)	0.75g
Na-disilicate monohydrate	3.0g
Sodium perborate monohydrate	1.16g
TAED granules (80% active)	0.72g
Oleic acid	0.20g
Alcalase 2.OT (23GU/ml)	0.075g
Termamyl 6.0 CM	0.20g

Termamyl is an amylase.

The formulations contained sodium dodecyl sulphate in amounts which were 0.75g, 1.5g and 3.0g.

Each formulation was used to wash various stained glass slides using a Bosch S510 automatic dishwasher on its standard program and without salt added to the machine. The main wash temperature was 55 °C, the final rinse temperature was 65 °C. The water used was tap water of 16° French Hardness.

The materials from which the various slides were made, the stains on them and the extent of removal are set out in the following table. In most instances the extent of removal was determined by weight loss. In a few instances the extent of removal was determined by visual inspection of the area which remains covered by the stain.

In addition the pressure delivered by the pump of the machine was monitored. This is a measure of the effectiveness of the defoamer, in that foaming leads to loss of pump pressure.

The results are set out in the following table. All of the wash solutions formed in the machine had a pH of 9.5.

Stain	Slide	wt% egg-yolk removal		
		0.75g SDS	1.50g SDS	3.00g SDS
egg-yolk	stainless steel	92 ± 9	100 ± 1	99 ± 2
egg-yolk	porcelain	92 ± 10	95 ± 0	100 ± 0
custard pudding	stainless steel	60 ± 26	33 ± 10	38 ± 16
custard pudding	porcelain	82 ± 13	73 ± 12	78 ± 14
potato	stainless steel *	97 ± 4	100 ± 1	100 ± 0
potato	porcelain *	85 ± 11	86 ± 10	93 ± 10
spinach	porcelain *	100 ± 0	100 ± 0	100 ± 0
Average pump pressure		90%	79%	70%

* denotes visual score

Example 14

A composition containing Dehypon KE 2429 foam inhibitor (believed to be a mixture of branched chain alcohol and ketone according to EP-A-324,339) was used to wash a stainless steel plate 20cm x 6cm with almost 0.8g baked-on egg-yolk, in a Bosch 5510 machine. The wash conditions were the same as for Example 12. The composition contained:

Sodium citrate dihydrate	5.0g
Sodium dodecyl sulphate	1.25g
Alcalase 2.OT	0.20g
Dehypon KE2429	0.50g

Removal of soil, determined as loss in weight, was 83%. Average pump pressure was 73% of pressure achieved with water only and no load in the machine.

Example 15

Example 14 was repeated while also including 0.50g oleic acid in the composition.

Removal of soil, determined as loss in weight, was 91%. Average pump pressure was 100% of the pressure achieved with water only and no load in the machine.

Example 16

Several machine dishwashing formulations were prepared. Each was a mixture containing:

	Amount by weight
Na-citrate dihydrate	3.0g
Acrylic-maleic copolymer (Sokolan CP5)	0.75g
Na-disilicate monohydrate	3.0g
Sodium dodecyl sulphate	2.5g
Oleic acid	0.17g
Ca-stearate/wax mixture	0.08g
Termamyl 6.OCM	0.20g

Various proteases were included in these formulations which were then used to wash porcelain and stainless steel slides stained with baked-on egg-yolk. The results, which are determined by loss in weight, are set out in the following table.

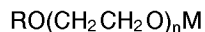
Protease	Activity in solution	wt% egg-yolk removal	
		steel	porcelain
Savinase 6.0CM	45GU/ml	68± 8	66± 9
Esperase 2.0T	40GU/ml	70±11	74±15
Alcalase CM1.5	45GU/ml	90± 6	91± 6

All of the active/protease combinations are compatible with amylases.

Claims

1. A chlorine bleach-free aqueous liquid machine dishwashing detergent composition comprising:
 - (a) from 0.0002 to 0.05 Anson units per gram of the composition of a proteolytic enzyme;
 - (b) from 5 to 90% by weight of a detergency builder.
 - (c) from 1 to 40% by weight of sodium or potassium silicate having $\text{SiO}_2:\text{Na}_2\text{O}$ or $\text{SiO}_2:\text{K}_2\text{O}$ ratio of from about 2.0 to about 3.2.
 - (d) from 3 to 50% by weight of an organic surfactant selected from the group of:

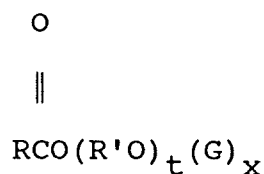
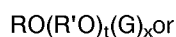
- (i) glycoside surfactants;
 (ii) anionic surfactants with a hydrophilic head group which is, or which contains a sulphate or sulphonate group and a hydrophobic portion which is or which contains an alkyl or alkenyl group of 8 to 22 carbon atoms;
 5 (iii) ethoxylated fatty alcohols of formula



where R is an alkyl group of 6 to 16 carbon atoms and n has an average value which is at least four and is sufficiently high that the HLB value of the ethoxylated fatty alcohol is 10.5 or greater, with the proviso that if ethoxylated fatty alcohol (iii) is used without anionic surfactant (ii) the majority of its alkyl groups R contain 6 to 12 carbon atoms; and
 (IV) mixtures thereof.

(e) water, said composition having pH of 7-11, if added to deionised water at a concentration of 2 g/l.

2. A composition according to claim 1 wherein the glycoside surfactant is of general formula

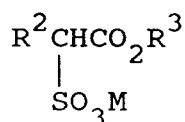


in which G is a residue of a pentose or hexose, R'O is an alkoxy group, x is at least unity and R is an organic hydrophobic group containing from 6 to 20 carbon atoms.

3. A composition according to claim 2, wherein R is alkyl or alkenyl of 7 to 16 carbon atoms and x has a value in the range from 1 to 1.8.
 4. A composition according to claim 1 wherein the anionic surfactant is selected from:
 primary alkyl sulphate of formula



where R' is a primary alkyl group of 8 to 18 carbon atoms and M is a solubilising cation,
 fatty acid ester sulphonate of formula

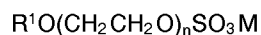


where R² is an alkyl group of 6 to 16 carbon atoms, R³ is an alkyl group of 1 to 4 carbon atoms and M is a solubilising cation,
 alkyl benzene sulphonate of formula



where R⁴ is an alkyl group of 10 to 16 carbon atoms and M is a solubilising cation,

alkyl ether sulphate of formula



5 where R^1 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 solubilising cation.

5. A composition according to any one of the preceding claims 1-4, which comprises from 5-25% by weight of said sodium or potassium silicate.

10 6. A composition according to claims 1-5, which comprises sodium silicate having $SiO_2:Na_2O$ ratio of at least 2.4.

15 7. A composition according to any one of the preceding claims 1-6, wherein the total quantity of surfactant is from 5 to 25% by weight.

8. A composition according to any of the preceding claims 1-7, further including a peroxygen bleach.

20 9. A composition according to any of the preceding claims 1-8, further including a defoamer other than a nonionic surfactant.

10. A composition according to any of the preceding claims 1-9, further including amylase and/or lipase.

25 11. A composition according to any of the preceding claims 1-10, having a pH of from 9.0 to 9.5.

12. A composition according to any of the preceding claims 1-11, wherein said detergency builder is a non-phosphate builder.

30 13. A method of washing crockery and/or glassware comprising exposing the crockery and/or glassware to a mixture of water and a detergent composition according to any one of the preceding claims.

35 14. Use of 3 to 50% by weight of the composition of an organic surfactant as defined in claim 1 as booster for protein soil removal in a machine dishwashing composition containing a proteolytic enzyme and a detergency builder.

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