PATENT SPECIFICATION (11) 1 572 605

1 572 605

(21) Applications No's 9258/76 (22) Filed 8 Mar. 1976
51465/76 9 Dec. 1976

(23) Complete Specification Filed 8 Mar. 1977

(44) Complete Specification Published 30 Jul. 1980

(51) INT. CL.[3] C11D 10/02
(C11D 10/02 1/83 3/20 3/43 3/386)

(52) Index at Acceptance
C5D 6A1 6A5D2 6A9 6B11A 6B11C 6B11D 6B12B1 6B12B2 6B12B3 6B12G1 6B12G2A 6B12N1 6B12N2 6B12N3 6B1 6B2 6B7 6B8 6C8

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(19)

(54) LIQUID ENZYME CONTAINING DETERGENT COMPOSITION

(71) We, THE PROCTER & GAMBLE COMPANY, a company organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:-

Liquid homogeneous, substantially unbuilt enzymatic detergent compositions are disclosed containing a surfactant mixture; a low level of a polyacid; free-calcium ions, a proteolytic enzyme and a liquid carrier mixture. These compositions are capable of providing superior cleaning performance and improved storage stability.

The present invention pertains to liquid homogeneous substantially unbuilt enzyme containing detergent compositions. These liquid compositions contain a major amount of a surfactant mixture comprising a nonionic ethoxylated surfactant and an anionic synthetic surfactant, a low level of a polyacid, free calcium ions, a proteolytic enzyme and a liquid carrier. The liquid compositions of this invention are from a performance standpoint comparable to granular built heavy duty detergent compositions. In respect to the comparable known liquid detergent state of the art, the compositions herein are capable of providing superior cleaning performance and excellent storage stability, particularly as regards the enzymatic activity.

To be satisfactory for washing or pre-treating and subsequent washing of heavily soiled fabrics, such as cotton and synthetic fabrics, liquid detergent compositions contain an adequate concentration of detergent compounds. In addition, they must remain stable and homogeneous when subjected to various storage conditions and be designed for use in both horizontal (tumble drum type) and upright (vertical agitator type) washing machines and for topical application as well as for handwashing.

Liquid, heavy duty detergent compositions containing a synthetic organic detergent compound, which is generally anionic, nonionic or mixed anionic-nonionic in nature; an inorganic builder salt; and a solvent, are disclosed, for example, in US patents 2,551,634; 1,908,651; 2,920,045; 2,947,702; 3,239,468; 3,272,753; 3,393,154; 3,554,916; 3,697,451; and 3,709,838; Belgian patents 613,165; 665,532; 794,713 and 817,267; British patents 759,877; and 842,813; and German published applications 1,617,119; 1,937,682; 2,327,861; 2,530,840; and 2,361,448 and 2,362,114. These compositions frequently contain a hydrotrope or solubilizing agent to permit the addition of sufficient quantities of surfactants and usual builder salts to provide a reasonable volume usage/performance ratio. Others are substantially anhydrous liquid compositions containing an alkanolamine component (US patent 3,528,925). Still others contain a soap component (US patents 2,875,153 and 2,543,744).

It is well-known that the formulation of enzyme containing liquid detergent compositions is a very delicate task due to the rapid decrease of the enzymatic activity in aqueous medium during storage. In fact, the difficulties flowing from the inherent losses in enzymatic activity are such that until now, this problem could not be solved satisfactorily. The significance of

these obstacles will even be better understood when considering that the desirability for formulating liquid detergent compositions containing enzymes is known for a good time already. The absence of any practical solution to this highly unsatisfactory enzymatic activity retention in aqueous detergent medium confirms all the more, both, the instability of enzymes in current liquid detergents compositions and concomitantly the difficulties for selectively formulating a liquid composition containing enzymes which might be of commercial interest.

The state of the art is scattered in respect of this particular aspect of detergent technology. So, for example, it is known from published Dutch patent application 66.08106 that proteolytic enzymes do only have a limited stability in aqueous medium. In addition to this, it is expressed that most detergent ingredients such as phosphate, carbonates, and sulfates have an adverse effect on the activity of these enzymes as well as on their stability in detergent solution. This reference amounts to an explanation why (proteolytic) enzymes are until now only incorporated into granular detergent compositions. No concrete solution however is suggested relative to the deficient stability.

From the disclosures of "BIOCHEMICA ET BIOPHYSICA ACTA", Vol. 6 (1950), pages 237 et seq., it is known that sequestering agents in general exert a destabilizing effect on proteolytic enzymes in aqueous medium. Citric acid, oxalic acid, ethylenediaminetetracetic acid, and nitrilotriacetic acid examplify this known destabilizing effect. German patent application DOS 2,301,728 is representative of the known prior art. It discloses that various enzyme preparations can be incorporated into liquid detergent compositions preferably in conjunction with detergent sequestering builders.

As can be seen from the foregoing, a substantial effort has been expanded in developing built and builder-free detergent compositions in liquid form. Yet, there are several problems associated with the art-disclosed compositions which render them less optimal for wide scale use, undesirable from an ecological standpoint in improperly treated sewage, objectionable from a performance point of view in cleaning both natural and synthetic fibers and subject to deactivation of the enzyme component during storage.

It has now been found that these known deficiencies can be avoided by formulating enzyme containing liquid detergent compositions' comprising a minor amount of a specific polyacid and a certain level of free calcium ions.

It has also been found that liquid, concentrated, heavy duty detergent compositions containing a major amount of a mixture of a polyethoxylated nonionic and an anionic synthetic surfactant in conjunction with a polyacid, a protease and the free calcium ions and having a pH in the range of from 6 to 7.5, exhibit superior removal of bleach-sensitive stains by topical application and through-the-wash fabric cleaning. These liquid, concentrated, heavy duty detergent compositions exhibit good physical properties, remain homogeneous and stable under severe storage conditions and stand the addition of many usual adjuvants.

It is an object of this invention to provide liquid, enzyme containing heavy duty detergent compositions which exhibit excellent cleaning and superior bleach-sensitive stain removal by topical application and through-the-wash fabric cleaning.

It is another object herein to provide liquid, concentrated and stable, heavy duty detergent compositions which retain an effective enzyme activity under prolonged storage conditions.

It is still another object herein to provide liquid, concentrated, homogeneous, stable, heavy duty detergent compositions acceptable from an ecological standpoint.

These and other objects can now be met as will be seen from the following disclosure.

It has now been discovered that homogeneous liquid, enzyme containing detergent compositions can be formulated which do provide significant advantages during storage and use. The liquid compositions claimed herein consist essentially of:

a) from 35% to 75% by weight of a surfactant mixture comprising an ethoxylated non-ionic surfactant and an anionic synthetic surfactant wherein the weight ratio of said non-ionic surfactant to said anionic surfactant is in the range from 1:1 to 5:1;

b) from 0.05 to 1.5% by weight of a polyacid capable of forming water-soluble Ca-complexes;

c) from 0.5 millimole/l to 15 millimoles/l of calcium ions;

d) from 0.001% to 2% of an alkaline proteolytic enzyme having an iso-electric point of greater than 8;

e) a liquid solvent system comprising water and from 2% to 15% by weight of a C_2 to C_6 aliphatic alcohol having 1 to 3 hydroxyl groups;

the pH of the composition being within the range from 6.0 to 7.5

In a preferred embodiment, the polyacid is present in an amount from 0.05% to 1.0% by weight, wherein said polyacid is capable of providing an enzyme stability which is about equivalent to the enzyme stability provided by adding from 0.3% to 0.6%, preferably 0.5% by weight citric acid, said stability for the polyacid and the citric acid being determined in

substantially identical compositions of this invention.

The logarithmic value of the stability constant of the Ca-complexes of the polyacid is preferably greater than 1.5, most preferably between 2.0 and 4.0 at the pH of the composition.

The term "free calcium ion" or "calcium ion" as used herein is meant to express calcium not bound by the polyacid (sequestering agent).

These essential components are described in more details hereinafter.

Unless indicated to the contrary, the percentage indications stand for percent by weight.

The surfactant mixture is used in an amount from 35% to 75%, preferably from 40% to 55%. Using less than 35% of the surfactant mixture may lead to stability problems, especially phase stability. The upper limit is dictated by homogeneity reasons i.e. using substantially more than 75% of the surfactant mixture can create difficulties for incorporating - dissolving - the enzyme component. The weight ratio of polyethoxylated nonionic surfactant to anionic synthetic surfactant is normally in the range of from 1:1 to 5:1, preferably from 1:1 to 3:1.

The nonionic ethoxylate can be represented by all known detergent ethoxylates which are known to be suitable for use in detergent technology. Such nonionic compounds are conventionally produced by condensing ethylene oxide, forming the hydrophilic moiety or ethenoxy chain, with a hydrocarbon having a reactive hydrogen atom, e.g., a hydroxyl-, carboxyl-, or amino group, and forming the hydrophobic moiety, in the presence of acidic or basic catalysts. Such procedures result in the production of a product mixture comprising a number of nonionics of varying ethoxylate content. Therefore, the conventional designation of the number of ethylene oxide units "m" present per molecule of nonionic compound as designated, for example, in the general formula $R\text{-}A(CH_2CH_2O)_mH$, wherein R represents the hydrophobic moiety and A the group carrying the reactive hydrogen atom, is an indication of the average number of ethylene oxide units per molecule of nonionic compound according to a statistic distribution where the peak is situated around the "m" number.

The properties of the polyethoxylated nonionics depend to a considerable extent on the hydrophilic moiety or average number of ethylene oxide units present. Most commercially available polyethoxylated nonionics are viscous liquids or soft pastes having in general from 2 to 24 ethylene oxide units in average.

The polyethoxylates nonionic detergent compounds useful in the compositions of the present invention include preferably those compounds which are obtained by reacting an alcohol with ethylene oxide and which are soluble in the instant liquid compositions.

Polyethoxylated nonionic compounds have a negative temperature coefficient of solubility in water, becoming less soluble at higher temperatures. Therefore, soluble in the instant liquid compositions means soluble at temperatures below 35°C.

Usually, the polyethoxylated nonionic detergent compounds are considered to include only those compounds which are soluble in water. There is a large number of polyethoxylated nonionic compounds having detersive properties but which do not have enough hydrophilic character to be fully soluble in water but are dispersible in water. They can be solubilized in water, however, with the help of solubilizing agents such as C_2-C_6 aliphatic alcohols, by admixing highly soluble polyethoxylated nonionic compounds or by hydrotropes. Therefore, soluble in the instant liquid compositions means soluble *per se* in water or soluble in the instant liquid composition.

The hydrophobic moiety of the nonionic compounds useful in the composition of the present invention can be derived from primary and secondary, straight or branched, saturated or unsaturated aliphatic alcohols having from 8 to 24, preferably from 12 to 20 carbon atoms. Another source is the alkylphenols wherein the alkyl group or groups have from 1 to 12 carbon atoms, wherein at least one group has at least 6 carbon atoms and the total number of carbon atoms in the alkyl groups is at most 15.

Primary alcohols can be derived from animal and vegetable oils and fats by, for example, hydrogenolysis of said oils, fats or corresponding fatty acids. They are substantially straight-chain or linear alcohols.

Primary alcohols can also be obtained from synthetic sources by different processes. The usual raw materials are polymers of lower alkylenes or olefins. According to the type of polymers, olefins, processes and process conditions, alcohols with a different degree of linearity or branching are obtained. The major part of the commercially available primary synthetic alcohols are prepared by either the "OXO" or "Ziegler" process.

Secondary alcohols are mostly obtained from synthetic sources, e.g., from olefins, either by direct hydration at high temperatures and pressures or hydrolysis of the intermediate sulfuric acid product; by oxidation of paraffins, etc.

Alkylphenols are obtained by reacting a phenol with an olefin thermally preferably in the presence of a catalyst, e.g., boron trifluoride. Xylenol and cresol can also be used instead of

phenol.

Preferred for the compositions of the present invention are polyethoxylated nonionics derived from primary and secondary aliphatic alcohols.

The hydrophilic moiety of the nonionic compounds useful in the composition of the present invention is an ethenoxy chain consisting of from 2 to 24 ethylene oxide units in average, depending upon hydrophobic character of the hydrocarbon group. Preferred are those ethenoxy chains containing at least about 4 ethylene oxide units.

Suitable examples of polyethoxylated nonionic compounds can, for example, be prepared from aliphatic primary alcohols containing from 12 to 20 carbon atoms condensed with from 4 moles to 14 moles of ethylene oxide per mole of alcohol. Non-limiting, specific examples of polyethoxylated nonionic detergent compounds derived from straight chain primary aliphatic alcohols are: $C_{12}H_{25}$-O-$(C_2H_4O)_6$-H; $C_{16}H_{33}$-O-$(C_2H_4O)_9$-H; $C_{18}H_{35}$-O-$(C_2H_4O)_9$-H; $C_{18}H_{37}$-O-$(C_2H_4O)_9$-H; $C_{14}H_{29}$-O-$(C_2H_4O)_9$-H; $C_{12}H_{25}$-O-$(C_2H_4O)_9$-H; $C_{12}H_{25}$-O-$(C_2H_4O)_4$-H; $C_{16}H_{33}$-O-$(C_2H_4O)_9$-H; tallow-O-$(C_2H_4O)_{11}$-H; $C_{11}H_{23}$-O$(C_2H_4O)_4$-H; $C_{16}H_{33}$-O$(C_2H_4O)_7$-H; and mixtures thereof. Non-limiting, specific examples of polyethoxylated nonionic detergent compounds derived from secondary aliphatic alcohols are: $C_{12}H_{25}CH(C_4H_9)$-O-$(C_2H_4O)_9$-H; $C_8H_{17}CH(C_4H_9)$-O-$(C_2H_4O)_{12}$-H; $(C_7H_{15})_2CH$-O-$(C_2H_4O)_6$-H; $C_{17}H_{35}CH(CH_3)$-O-$(C_2H_4O)_9$-H; $C_{14}H_{29}CH(C_3H_7)$-O-$(C_2H_4O)_9$-H; $C_{14}H_{29}CH(CH_3)$-O-$(C_2H_4O)_9$-H; and mixtures thereof. Non-limiting, specific examples of polyethoxylated nonionic detergent compounds derived from branched primary aliphatic alcohols are: $C_{10}H_{23}CH(CH_3)CH_2$-O-$(C_2H_4O)_9$-H; $C_{12}H_{25}CH(CH_3)CH_2$-O-$(C_2H_4O)_{11}$-H; $C_{15}H_{31}CH(CH_3)CH_2$-O-$(C_2H_4O)_9$-H; $C_{13}H_{27}CH(CH_3)CH_2$-CH_2-CH_2-O-$(C_2H_4O)_9$-H; $C_{12}H_{25}CH(C_2H_5)$-CH_2-O-$(C_2H_4O)_9$-H; $(C_7H_{15})_2CH$-CH_2-O-$(C_2H_4O)_{12}$-H; $C_9H_{19}CH(C_8H_{17})CH_2$-O-$(C_2H_4O)_{12}$-H; $C_{13}H_{27}CH(C_4H_9)CH_2$-O-$(C_2H_4O)_{11}$-H; $C_{13}H_{27}CH$-$(C_3H_7)CH_2$-CH_2-O-$(C_2H_4O)_9$-H, and mixtures thereof. Non limiting, specific examples of polyethoxylated nonionic detergent compounds derived from alkylphenols are $C_9H_{19}C_6H_4$-O-$(C_2H_4O)_9$-H; $C_{12}H_{25}C_6H_4$-O-$(C_2H_4O)_{12}$-H; $(C_9H_{19})(CH_3)C_6H_3$-O-$(C_2H_4O)_{12}$-H; $(C_{12}H_{25})(CH_3)_2C_6H_2$-O-$(C_2H_4O)_{11}$-H; $C_{12}H_{25}C_6H_4$-O-$(C_2H_4O)_6$-H; and mixtures thereof. Non-limiting, specific examples of mixtures of polyethyoxylated nonionic compounds consisting of slightly water-soluble and highly water-soluble nonionics useful in the compositions of the present invention are: 1/2 mixture of $C_{12}H_{25}$-O-$(C_2H_4O)_5$-H and $C_{12}H_{25}$-O-$(C_2H_4O)_{12}$-H; 1/1 mixture of $C_{14}H_{29}$-O-$(C_2H_4O)_5$-H and tallow-O-$(C_2H_4O)_{11}$-H; 2/1 mixture of $C_{15}H_{31}$-O-$(C_2H_4O)_7$-H and tallow-O-$(C_2H_4O)_{11}$-H; 1/4 mixture of $C_{10}H_{21}$-O$(C_2H_4O)_3$-H and $C_{13}H_{27}CH(CH_3)CH_2$-O-$(C_2H_4O)_{10}$-H; 1/1/1 mixture of $C_8H_{17}CH(C_6H_{13})$-O-$(C_2H_4O)_6$-H; $C_{12}H_{25}CH(CH_3)CH_2$-O-$(C_2H_4O)_4$ and $C_{18}H_{37}$-O-$(C_2H_4O)_{15}$-H; 0.2/1/2 mixture of $C_9H_{19}C_6H_4$-O-$(C_2H_4O)_9$-H; $C_{15}H_{31}$-O$(C_2H_4O)_5$-H and $C_{18}H_{37}$-O-$(C_2H_4O)_{12}$-H; 2/1/1 mixture of $(CH_3)_3C(CH_2)_8CH_2$-O-$(C_2H_4O)_3$-H; $C_{16}H_{33}CH(CH_3)CH_2$-O-$(C_2H_4O)_{11}$-H and $C_{14}H_{29}CH(CH_3)$-O-$(C_2H_4O)_9$-H (all ratios being by weight).

A particularly preferred nonionic surfactant is represented by a mixture of: (1) a primary aliphatic alcohol ethoxylate obtained from an alcohol, the hydrocarbyl chain of which contains at least 65% branched-chain structure and is obtained by hydroformylation of random olefins and has from 14 to 22, especially from 16 to 19 carbon atoms in the hydrocarbyl chain, and 8 to 14 moles of ethylene oxide; and (2) an alcohol ethoxylate derived from a primary alcohol with preferably 40% branched-chain structure and having from 9 to 15, especially from 12 to 15 carbon atoms in the hydrocarbyl chain, and 3 to 7 moles of ethylene oxide. Another preferred species of the C_9-C_{15} ethoxylated alcohol has about 60% branched chain structure.

The essential anionic surfactant can be represented by the general formula

$$R_3SO_3M$$

wherein R_3 represents a hydrocarbyl group selected from straight or branched alkyl radicals having from 12 to 24 carbon atoms; and alkylphenyl radicals having from 9 to 15 carbon atoms in the alkyl group; and M is a salt-forming cation selected from Na, K, NH_4, and mono-, di-, and trialkanol amines having 2 to 3 carbon atoms in the alkanol groups.

The preferred anionic surfactant component of the instant detergent composition is a water-soluble salt of an alkylbenzene sulfonic acid, preferably an alkanolamine alkylbenzene sulfonate, having from 12 to 15 carbon atoms in the alkyl group.

More specifically, the preferred anionic surfactant herein consists of a mono-, di-, or triethanolamine salt of a straight chain alkylbenzene sulfonic acid in which the alkyl group contains in average about 12 carbon atoms.

The preferred alkanolamine alkylbenzene sulfonate salts are prepared by neutralizing the alkylbenzene sulfonic acid with an alkanolamine selected from the group consisting of mono-, di-, and triethanolamine. The triethanolamine salts are preferred herein.

Specific examples of alkanolamine salts of alkylbenzene sulfonic acids useful in the instant invention include triethanolamine decyl benzene sulfonate, triethanolamine dodecyl benzene sulfonate, diethanolamine undecyl benzene sulfonate, monoethanolamine tridecylbenzene sulfonate, triethanolamine tetradecyl benzene sulfonate, and mixtures thereof.

Other anionic surfactants useful herein include the organic sulfuric acid reaction products having in their molecular structure an aliphatic hydrocarbon group containing from 12 to 24 carbon atoms, or mixtures thereof. Examples of this group of synthetic detersive anionic surfactants are the paraffin sulfonates, especially the secondary paraffin sulfonates having in average 13 to 16 carbon atoms; and olefin sulfonates. The anionic surfactants are used in the form of their sodium, potassium, ammonium, but preferably in the form of their mono-, di-, and triethanolamine salts, or mixtures thereof.

A preferred surfactant mixture for use herein comprises a nonionic surfactant produced by the condensation of from 2 to 4 moles of ethylene oxide and one mole of an aliphatic alcohol containing from 14 to 16 carbon atoms. and an anionic synthetic surfactant neutralized with an alkanolamine.

Another preferred surfactant mixture for use in the compositions of this invention comprises a nonionic surfactant produced by the condensation of alkylene oxide with an organic compound having a hydrophilic-lipophilic balance of from 8 to 15; and an ethanolamine alkylbenzene sulfonate having from 9 to 15 carbon atoms in the alkyl chain, the weight ratio of the nonionic surfactant to the anionic surfactant in its free acid form being in the range from 2.5:1 to 3.5:1.

Another essential component in the compositions of this invention is a polyacid capable of forming water-soluble calcium complexes; it is used in an amount from 0.05% to 1.5% preferably from 0.05% to 1%, and most preferably from 0.1% to 0.8%. Preferred polyacid species can be defined in the stability constant of their water-soluble Ca-complexes and by means of the enzyme stability of detergent compositions containing the polyacid versus what is achieved from an identical composition wherein the polyacid is citric acid which is present in an amount from 0.3 to 0.6%, preferably 0.5%.

The logarithmic value, at the pH of the detergent composition, of the stability constant of the water-soluble calcium complexes of preferred polyacids is greater than 1.5, most preferably in the range from 2.0 to 4.0 (at the pH of the detergent composition).

The stability constant qualifies those polyacids, which although capable of providing calcium sequestring power in the detergent composition will leave therein a certain amount of free calcium ions. A total sequestration of the free calcium can lead to a certain deactivation of the enzyme which thus is expressed in terms of decreased stability, for example, by reference to an identical composition which comprises from 0.3% to 0.6%, preferably 0.5% citric acid.

The water-soluble Ca-complexes of suitable polyacids have a logarithmic stability constant greater than 1.5, preferably in the range from 2.0 to 4.0. These constants are determined at a temperature in the range from 10°C to 40°C. The stability constants are known as "conditional stability constants" of the calcium complexation at a given pH. They can be calculated in accordance with : COMPLEXATION in ANALYTICAL CHEMISTRY" by A. Ringbom, Edit. Interscience Publisher. Additional reference is directed to "STABILITY CONSTANTS" published by the London Chemical Society, 1964.

Suitable polyacids are additionally defined by means of the enzyme stability in a composition of this invention versus what is obtained from an identical composition wherein the polyacid is replaced by citric acid in a level from 0.3 to 0.6%, preferably 0.5%. The liquid detergent compositions of this invention which do not contain a polyacid, can be used as base-liquid to select, qualitatively and quantitatively, suitable polyacids for use herein. The following description examplifies the polyacid selection.

A liquid detergent composition is prepared by mixing the following ingredients:

	in %
– triethanolamine salt of a linear alkylbenzene sulfonic acid, wherein the alkyl chain averages 11.7 carbon atoms in length	20
– condensation product of branched (72%) fatty alcohol having from 16 to 19 carbon atoms in the alkyl chain and 11 moles of ethylene oxide	20
– condensation product of branched (60%) fatty alcohol having from 12 to 15 carbon atoms in the alkyl chain and 4 moles of ethylene oxide	10

– ethanol	10
– optical brightener (Stilbene type)	0.25
– triethanolamine salt of saturated fatty acid having in average 16-22 carbon atoms	0.75
– triethanolamine (free)	1 to 2 to adjust pH of composition (as is) at pH 7
– proteolytic enzyme (commercial enzyme preparation containing 15% pure enzyme)	0.4
– polyacid	see below
– water	balance to 100%

The above liquid composition contains about 4 millimoles/liter of the composition of calcium originating mostly from the commercial enzyme preparation with adjustment if needed.

Candidate polyacids for use in this invention and citric acid at a level of e.g. 0.5% are added to separate samples of the above detergent composition. These samples are submitted to an accelerated storage test at 45°C ± 1°C for 40-60 hours or at 35°C ± 1°C for 2 weeks. The residual enzymatic activity is analyzed thereby using the method described in : "ANALYST", 96, pages 159-163 (1973), E. DUNN and R. BROTHERTON".

A control sample which does neither contain a polyacid nor citric acid is carried along. A selected polyacid, species and level, is suitable for use in the compositions of this invention if the residual enzymatic acitivity is of the same order of magnitude as the residual enzymatic activity of the sample containing citric acid and/or the control which does not contain a polyacid. It is understood that the Ca-complexes of the polyacid are water-soluble i.e. the detergent composition will be substantially free of precipitates and/or cloudiness. The selection technique requires a suitable level of free-calcium in the range from 0.05 to 15 millimoles. Part of the free-calcium serves to achieve enzyme-stability. The minimum enzyme levels claimed i.e. 0.001% require less than 0.5 millimole Ca-ions.

The following polyacids were tested in accordance with the procedure described hereinbefore. The storage test conditions were : 35°C - 2 weeks. The residual enzyme stability is calculated by reference to the initial activity for a given sample being 100%.

Polyacid species	%	Appearance of detergent composition	Residual enzyme activity %	Logarithmic value of stability constant of polyacid Ca-complexes at pH 7
-none (control)	0.0	cloudy	65	not applicable
-malic acid	0.5	cloudy	80	1.0
-nitrilotriacetic acid	0.5	clear	75	3.5
-citric acid	0.5	clear	68	3.5
-ethylenediamine tetramethylenephosphonic acid	0.5	clear	66	–
-diglycolic acid	0.2	clear	67	2.0
-tripolyphosphoric acid	0.5	clear	12	4.5

-ethylenediamine tetraacetic acid	0.5	clear	0	7.2
-ethylenediamine tetraacetic acid	0.07	clear	62	7.2

Detergent composition used in selecting suitable polyacids as described above except that the level of total calcium is increased to 8 millimoles:

-ethylenediamine tetraacetic acid	0.25	clear	68	7.2

This data shows that the enzyme stability for a given level of polyacid (0.5%) is inversely related to the logarithmic stability constant of the Ca-polyacid complexes at the pH of the composition. The logarithmic stability constant being a measure of Ca-sequestering ability, it thus can be concluded that relatively strong sequestrants at the given pH shall be incorporated in an amount which will leave a minimum level, as defined herein, of free calcium ions in the composition. Weak sequestrants having a logarithmic stability constant of less than 1.5, although capable of providing enzyme stability, do not procure a homogeneous (and clear) liquid composition. Strong sequestrants to provide the advantages of this invention need, of course, a higher level of total calcium in the composition.

As is apparent from the above, citric acid can advantageously be used to select, qualitatively and quantitatively, suitable polyacid species.

The preferred polyacids having a logarithmic stability constant in the range from 2.0 to 4.0 in addition to product appearance and enzyme stability also provide significantly improved cleaning performance, particularly on bleach and builder sensitive stains as more fully explained in concurrently filed patent application No. 9257/76 serial No. 1569617 entitled: "LIQUID DETERGENT COMPOSITION" - inventors : J. ARNAU, C. BARRAT and J. WEVERS. Docket number : CM-1

A broad class of preferred polyacid species for use in the compositions of this invention is comprised of organo-phosphonic acids, particularly alkylene-polyamino-polyalkylene phosphonic acids, inclusive of ethylenediamine tetramethylene phosphonic acid; hexamethylene diaminetetramethylene phosphonic acid, diethylene triaminepentamethylene phosphonic acid; and amino-trimethylene phosphonic acid. Additional preferred polyacid species include: nitrilotriacetic acid; citric acid; and diglycolic acid. Suitable polyacids can be incorporated into the compositions herein in the form of their acids, acid salts or salts.

The liquid detergent compositions of this invention comprise from 0.5 to 15, preferably from 1.5 to 10 millimoles (m-mol) of free calcium ions. The free calcium ions are either originating from their presence in the additional components of this invention, especially the enzyme preparation, or can be added directly into the compositions. The latter can be achieved by utilizing an aqueous solution of any commonly available calcium salts such as chloride and acetate. The level of free calcium ions can be determined by known methods or can easily be calculated from the logarithmic stability constant of the polyacid at the pH of the composition.

The essential enzyme components is represented by an alkaline protease having an isoelectric point of greater than 8. The enzyme is present in an amount from 0.001% to 2%, preferably from 0.005% to 0.8%, especially from 0.02% to 0.2%.

The alkaline proteases herein have an iso-electric point greater than 8. The iso-electric point, can be determined by electrophoresis on agarose thereby using the technique described by R.J. WIEME, in AGAR GEL ELECTROPHORESIS, Elsevier Publ. Comp. 1965. "Greater" with respect to the numerical value of the iso-electric point refers to the absolute value of the iso-electric point. The most preferred proteolytic enzyme preparations for use in this invention are derived from bacillus subtilis such as for example ALCALASE - registered Trade Made - manufactured by NOVO INDUSTRI A/S, and MAXATASE - registered Trade Mark - manufactured by GIST-BROCADES N.V. The Netherlands. These most preferred enzyme species have an iso-electric point in the range from 8.5 to 9.2.

An essential condition of the present invention is that the compositions have a pH within the range of from 6 to 7.5, preferably between 6.0 and 7.

Compositions containing the essential components of the present invention but having a pH below 6 can present processing difficulties, especially in respect to the incorporation of stilbene-type brightener.

Compositions containing the essential components but having a pH above 7.5 do not

anymore provide the full benefits of the invention.

The liquid, organic carriers or solvents, which should not chemically react with any of the components of the instant compositions, are selected from aliphatic alcohols having from 2 to 6 carbon atoms and 1 to 3 hydroxyl groups; and mixtures thereof. The organic co-solvent usually represents from 2%-15% of the detergent composition.

Suitable examples of C_2-C_6 aliphatic alcohols useful in the instant compositions are ethanol, n-propanol, isopropanol and butanol; 1,2-propanediol, 1,3-propanediol, and n-hexanol.

Hydrotropes that can be used in the instant compositions are the water-soluble alkylaryl sulfonates having up to 3 carbon atoms in an alkyl group such as sodium, potassium, ammonium and ethanol amine salts of xylene-, toluene-, ethylbenzene- and isopropylbenzene sulfonic acids.

They are preferably used in compositions containing, in addition, an organic, synthetic, anionic surfactant of the sulfonate type.

A desirable component for addition herein can be represented by a suitable opacifier. It contributes to create a uniform aesthetical appearance of the subject technology on commercialization. Examples of suitabfle opacifiers include polystyrene commercially known as LYTRON 621 and LYTRON 607 manufactured by MONSANTO Chemical Corporation. It has been found that the LYTRON opacifiers can be incorporated in the compositions of this invention only in presence of the polyacid i.e., the opacifier precipitates in the compositions herein which do not contain the polyacids.

Optional components include brighteners, fluorescers, antimicrobial agents, suds-regulating agents (inclusive of suds-suppressors and suds-boosters) and perfumes.

Such components preferably comprise not more than 5% by weight of the total compositions. One particular advantage of the instant compositions is that the hardly water-soluble brighteners and fluorescers can be added either directly to the compositions, i.e., as such, or during any step of the formulation process.

The suds-suppressors can be represented by substantially hydrogenated fatty acids having from 16 to 24 carbon atoms in the hydrocarbyl chain, for example, hydrogenated fish oil, and/or by a silicone suds suppressant as for example described in pending British patent application No serial 57/76, No 1562801 entitled "Liquid Detergent Composition" filing date 2nd January 1976, incorporated herein by reference.

Additional examples illustrating the invention are described hereinafter.

Ingredient	Composition (in %)	
	A	B
– triethanolamine salt of a linear alkylbenzene sulfonic acid wherein the alkyl chain averages 11,7 carbon atoms	20	20
– condensation product of branched (72%) fatty alcohol having from 16 to 19 carbon atoms in the alkyl chain and 11 moles of ethylene oxide	20	–
– condensation product of branched (60%) fatty alcohol having from 12 to 15 carbon atoms in the alkyl chain and 4 moles of ethylene oxide	10	–
– proteolytic enzyme (MAXATASE, 15% pure enzyme)	0.4	0.4
– condensation product of 1:1 blend of C_{14}-C_{15} fatty alcohol and 7 moles of ethylene oxide	–	30
– ethanol	10	10
– optical brightener (Stilbene type)	0.25	0.25

– triethanolamine (free)	-------- 1 to 2 ---------- to adjust composition to	
	pH: 7	pH: 6.5
– 9:1 mixture of dimethylpolysiloxane and aerogel silica emulsified in ethoxylated fatty acid (DOW CORNING : DB 31)	0.1	0.2
– Water	----- Balance to 100 ----	

These liquid detergent compositions contained 4 millimoles/litre of calcium ions originating from the enzyme preparation.

Samples of above composition A and B were complemented through the addition of a polyacid :

	- Composition -					
	A			B		
	1	2	3	1	2	3
– citric acid	0.5	–	–	0.50	–	–
– ethylenediamine tetramethylene phosphonic acid	–	0.35	–	–	0.35	–

The testing results (accelerated storage 45°C: 36 hours) were as follows:

	Composition					
	A			B		
	1	2	3	1	2	3
residual enzyme activity	42	44	38	66	54	52
product appearance	clear	clear	cloudy	clear	clear	cloudy
performance on bleach-sensitive stains	4.5	4.8	3.9	3.45	4.5	2.8

The performance on bleach-sensitive stains was assessed by visual examination by reference to a scale from 0 to 5 whereby 0 indicates no removal and 5 complete removal. The method is fully described in concurrently filed patent application no. 9257/76 serial no. 1569617 already referred to previously.

In respect to the above results, it is noteworthy that the performance on bleach-sensitive stains for composition $A_{1:2}$ and $B_{1:2}$ is significantly superior over what is obtained from A_3 and R_3 which do not contain the combination of enzyme and polyacid.

A liquid detergent composition was prepared by mixing the following ingredients :

Ingredients	Composition A in %
– triethanolamine salt of a linear alkylbenzene sulfonic acid, wherein the alkyl chain averages 11.7 carbon atoms in length	20
– condensation product of branched(72%) fatty alcohol having from 16 to 19 carbon atoms in the alkyl chain and 11 moles of ethylene oxide	20
– condensation product of branched(60%)fatty alcohol having from 12 to 15 carbon atoms in the alkyl chain and 4 moles of ethylene oxide	10

– ethanol	10
– optical brightener (Stilbene type)	0.25
– proteolytic enzyme (commercial enzyme preparation containing 15% pure enzyme)	0.4
– 9:1 mixture of dimethylpolysiloxane and aerogel silica emulsified in C_{12}-C_{16} fatty acid - ethoxylated	0.1
– free triethanolamine	1 to 2 (adjust to pH 7)
– water	balance to 100
– calcium ions	4 millimoles/litre of composition

Polyacids were added to composition A in the amounts indicated. The composition was then evaluated for product appearance and residual enzyme active thereby using the techniques applied in the preceding example.

The testing results were :

	A		
Polyacid	1	2	3
no polyacid	0	–	–
ethylenediaminetetramethylene phosphonic acid	–	0.35%	–
nitrilotriacetic acid	–	–	0.75%
storage : 65 hours at 45°C			
residual enzyme activity	24	27	36
product appearance	cloudy	clear	clear

Identical compositions were prepared wherein the suds regulating system in addition to the silicone component contained from 0.05% to 1%, preferably from 0.2% to 0.7% of a substantially hydrogenated fatty acid having from 16 to 24 carbon atoms in the fatty alkyl (hydrocarbyl) chain. These compositions comprising the silicone/saturated fatty acid suds regulator do provide the inventive benefits of this invention. The silicone co-suds regulating component is normally present in an amount of up to 0.5%, preferably from 0.01% to 0.2%.

It is noteworthy that in presence of the pre-emulsified silicone/fatty acid suds regulating system, the free-calcium will not react with the fatty acid to thus form unsightly precipitates in the claimed compositions.

The following liquid detergent composition was prepared by mixing the ingredients in the specified amounts.

Ingredients	Composition (in %)
– triethanolamine salt of a linear alkylbenzene sulfonic acid wherein the alkyl chain averages 11.7 carbon atoms	20
– condensation product of branched(72%) fatty alcohol having from 16 to 19 carbon atoms in the alkyl chain and 11 moles of ethylene oxide	20

– condensation product of branched(60%) fatty alcohol having from 12 to 15 carbon atoms in the alkyl chain and 4 moles of ethylene oxide	10
– proteolytic enzyme (MAXATASE, 15% pure enzyme)	0.4
– ethanol	10
– optical brightener (Stilbene type)	0.25
– triethanolamine (free)	1 to 2
	to adjust to pH 7
– 9:1 mixture of dimethylpolysiloxane and aerogel silica emulsified in highly ethoxylated fatty acid (DOW CORNING : DB 31)	0.1
– water	balance to 100

The finished detergent composition contains 4 millimoles calcium ions originating from the proteolytic enzyme preparation.

Varying levels of polyacids were added as listed : the residual enzyme activity and the product appearance after 36 hours at 44°C were as follows :

Polyacid	%	residual enzyme activity (in % of initial activity)	Product appearance
Ethylenediaminetetramethylenephosphonic acid (EDTMP)	0.35	49	clear
citric acid	0.50	36	clear
EDTMP + citric acid	0.3 0.2	58	clear
none	–	33	cloudy

A liquid detergent composition according to this invention was prepared by mixing the following ingredients :

Ingredient	Composition (in %)
-linear alkyl benzene sulfonic acid (alkyl chain averages 11.7 carbon atoms in length)	13.7
-triethanolamine	8.5
-condensation product of branched (72%) fatty alcohol having from 16 to 19 carbon atoms in the alkyl chain, and 11 moles of ethylene oxide	20.0
-condensation product of branched (60%) fatty alcohol having from 12 to 15 carbon atoms in the alkyl chain and 4 moles of ethylene oxide	10.0
-proteolytic enzyme (Maxatase-containing 1.5 Anson unit/gram)	1.0

-ethanol	10.0
-C_{18}-C_{24} saturated fatty acid	0.5
-9:1 mixture of dimethylpolysiloxane and aerogel silica emulsified in ethoxylated fatty acid	0.1
-total calcium	see below
-polyacid	see below
-water and minors inclusive of pH 7 regulator and brightener	balance of 100

The compositions of this invention were completed by adding polyacids and by adjusting the total calcium to reach the levels indicated.

	Polyacid	%	Total Calcium (millimoles)
a)	no	–	4
b)	no	–	8
c)	Citric acid	1	10
d)	Citric acid EDTMP	0.5 0.5	6
e)	EDTMP	1	5
f)	Citric acid	0.5	5
g)	Diethylene triamine pentamethylene-phosphonic acid	1	10
h)	Hexamethylene diamine tetramethylphosphonic acid	0.5	4

It was found that the compositions of this invention (c through h) were free of precipitates whereas prior art compositions were cloudy. The residual enzymatic activity (under accelerated storage conditions 2 weeks; 35°C) of inventive compositions c-h was significantly superior over what was found for state of the compositions a and b.

WHAT WE CLAIM IS:-

1. A homogeneous liquid substantially unbuilt enzymatic detergent composition having enhanced cleaning performance and storage stability, consisting essentially of :

a) from 35% to 75% by weight of a surfactant mixture comprising an ethoxylated non-ionic surfactant and an anionic synthetic surfactant wherein the weight ratio of said non-ioninc surfactant to said anionic surfactant is in the range from 1:1 to 5:1;

b) from 0.05% to 1.5% by weight of a polyacid capable of forming water-soluble Ca-complexes;

c) from 0.5 millimole to 15 millimoles/liter of composition of free calcium ions;

d) from 0.001% to 2% by weight of an alkaline proteolytic enzyme having an iso-electric point of greater than 8;

e) a liquid solvent system comprising water and from 2% to 15% by weight of a C_2 to C_6 aliphatic alcohol having 1 to 3 hydroxyl groups;

the pH of the composition being within the range from 6.0 to 7.5.

2. The composition in accordance with claim 1 wherein said polyacid is present in an amount from 0.05% to 1.0% by weight, said polyacid being capable of providing an enzyme stability which is about equivalent to the enzyme stability provided by adding from 0.3-0.6%, particularly 0.5% by weight citric acid, said enzyme stability for the polyacid and the citric acid being determined in substantially identical compositions of this invention.

3. The composition in accordance with claim 2 wherein the calcium complexes of the polyacid have a stability constant the logarithmic value of which is above 1.5 at the pH of the composition.

4. The composition in accordance with any one of the preceding claims wherein the surfactant mixture is present in an amount from 40% to 55% by weight, the weight ratio of said nonionic surfactant to said anionic surfactant being in the range from 1:1 to 3:1.

5. The composition in accordance with any one of the preceding claims wherein the free-calcium ions are present in an amount from 1.5 millimoles to 10 millimoles.

6. The composition in accordance with any one of the preceding claims wherein the proteolitic enzyme is present in an amount from 0.005% to 0.8% by weight.

7. The composition in accordance with any one of the preceding claims which in addition comprises a suds regulating system consisting of : (a) from 0.01% to 0.2% by weight of silicone; and (b) from 0.05% to 1% by weight of a saturated fatty acid having from 16 to 24 carbon atoms in the fatty alkyl chain.

8. The composition in accordance with any one of the preceding claims wherein the polyacid is selected from ethylenediamine tetramethylenephosphonic acid; hexamethylene diaminetetramethylenephosphonic acid; diethylene triaminepentamethylenephosphonic acid; and aminotrimethylenephosphonic acid.

9. The composition in accordance with claim 1 substantially as hereinbefore described specifically.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,from which copies may be obtained.