

- [54] **ENZYME-CONTAINING LIQUID DETERGENT COMPOSITIONS**
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[56] **References Cited**

UNITED STATES PATENTS

3,332,876	7/1967	Walker	252/152
3,332,880	7/1967	Kessler et al.....	252/161
3,325,364	6/1967	Merritt et al.....	167/73

FOREIGN PATENTS OR APPLICATIONS

1,678,837	6/1969	South Africa
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[57] **ABSTRACT**

Liquid detergent compositions comprising a mixture of from about 2 percent to about 35 percent of an alkane sulfonate, alpha-olefin sulfonate, or mixtures thereof having from about 10 to about 26 carbon atoms in the hydrocarbon chain; from about 2 percent to about 30 percent of an ethoxylated alcohol or alkyl phenol or sulfate thereof; and from about 0.001 percent to about 5.0 percent of enzyme. The detergent compositions have desirable enzyme activity upon storage and exhibit desirable levels of soil-removal performance.

6 Claims, No Drawings

ENZYME-CONTAINING LIQUID DETERGENT COMPOSITIONS

This invention pertains to liquid detergent compositions containing enzymes, particularly proteases.

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 of formulating liquid detergent compositions containing enzymes has long been known. The absence of any practical solution to this highly unsatisfactory enzymatic activity retention in aqueous detergent medium confirms all the more the difficulties in selectively formulating liquid detergent compositions containing enzymes which might be of commercial interest.

THE PRIOR ART

The state of the art is scattered with respect to this particular aspect of detergent technology. So, for example, it is known from Dutch Pat. application No. 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 phosphates, 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. South African Pat. specification No. 67/6837 pertains to dishwashing compositions containing detergent active compounds, builders and amylases. The compositions, can, among others, be in liquid state but in that event, they contain alcohol in admixture with nonionics as stabilizing agent for the amyolytic activity. This use of alcohols, if desired, in admixture with nonionics as stabilizing agents for certain enzymes is also known from Dutch Pat. application No. 68.16356.

SUMMARY OF THE INVENTION

It has now been found that enzyme containing liquid detergent compositions can be prepared having an unexpected storage stability and an unforeseeable soil-removal performance versus what can be obtained from enzyme-containing liquid detergent compositions currently known. These inventive liquid detergent compositions comprise a mixture of

- from about 2 percent to about 35 percent by weight of alkane sulfonates or alpha-olefin sulfonates or mixtures thereof, both having from about 10 to about 26 carbon atoms in the hydrocarbon chain;
- from about 2 percent to about 30 percent by weight of a compound having the general formula:



- wherein A represents an alkyl chain with from eight to 30 carbon atoms or an alkyl phenyl with from three to 22 carbon atoms in the alkyl chain; E an alkyleneoxy radical, n an integer from one to 30 and X represents either hydroxyl, or a sulfate radical; and
- from about 0.001 percent to about 5.0 percent by weight of enzyme.

DETAILED DESCRIPTION OF THE INVENTION

Ingredient AE_nX should be present in an amount from about 2 percent to about 30 percent by weight and preferably from about 5 percent to about 20 percent by weight. The lower limit reflects minimum perceptible performance while the 30 percent upper limit has been set so that any additional incorporation of AE_nX is only likely to result in an expected performance increase. The radical A can be an alkyl chain with from about eight to about 30 carbon atoms, preferably

from about 10 to about 16 carbon atoms. In the event A is an alkyl phenyl radical, the alkyl group should contain from about three to about 22 carbon atoms, and preferably from about six to about 12 carbon atoms. E represents a poly(alkyleneoxy) radical preferably derived from ethylene oxide or propylene oxide or mixtures of both, while n stands for an integer in the range from one to 30, preferably two to 18. X represents either a hydroxyl or a sulfate radical.

The preferred surface-active agents, corresponding to the general formula AE_nX , suitable for being used in the compositions claimed are derived from the condensation products of fatty alcohols with from about two to about 18 moles of ethylene oxide, either bearing a terminal hydroxyl radical or being present in its sulfated form. Particularly preferred are the alkali metal and ammonium salts of the sulfated condensation product of one mole of a mixture of straight chain C_{12} to C_{14} alcohols with three moles of ethylene oxide.

The percent compositions should contain from about 2 percent to about 35 percent by weight, preferably from about 10 percent to about 25 percent by weight, of alkane sulfonates or alpha-olefin sulfonates or mixtures thereof, both having from about 10 to about 26 carbon atoms, preferably from about 12 to about 20 carbon atoms in the hydrocarbon chain. The alkane sulfonates (paraffin sulfonates) can, for example, be prepared by the sulfoxidation process. The reaction product obtained from that process after neutralization and purification steps at temperatures in the range from 200° C to 300° C is present as an anhydrous melt having about the following compositions: alkane mono-sulfonates, from 81 to 83 percent; alkane disulfonates, from 10 to 12 percent; non-reacted paraffin, 1 percent; sodium sulfate, about 6 percent. The preferred alkane sulfonate of this invention has the following chain distribution: C_{13} alkane sulfonate: 5 percent; C_{14} alkane sulfonate: 16 percent; C_{15} alkane sulfonate: 30 percent; C_{16} alkane sulfonate: 30 percent; C_{17} alkane sulfonate: 15 percent; C_{18} alkane sulfonate: 4 percent. The alkane sulfonates used in all the Examples correspond to this composition.

The preferred olefin sulfonate actives are described in detail in U.S. Pat. No. 3,332,880 issued July 25, 1967 to Kessler et al. They consist of a mixture of from about 30 to 70 percent of Component A, preferably 35 to 65 percent; about 20 to 70 percent of Component B, preferably 25 to 60 percent; and about 2 to 15 percent of Component C, preferably 3 to 12 percent.

Component A is a mixture of double-bond positional isomers of water-soluble salts of alkene-1-sulfonic acids containing from about 10 to about 24 carbon atoms, said mixture of positional isomers including about 10 percent to about 25 percent of an alpha-beta unsaturated isomer, about 30 percent to about 70 percent of a beta-gamma unsaturated isomer, about 5 percent to about 25 percent of a gamma-delta unsaturated isomer, and about 5 percent to about 10 percent of a delta-epsilon unsaturated isomer. Component B is a mixture of water-soluble salts of bifunctionally-substituted sulfur-containing saturated aliphatic compounds containing from about 10 to about 24 carbon atoms, the functional units being hydroxy and sulfonate radicals with the sulfonate radical always being on the terminal carbon and the hydroxyl radical being attached to a carbon atom at least two carbon atoms removed from the terminal carbon atom, at least 90 percent of the hydroxy radical substitutions being in the 3-, 4-, and 5- positions. Component C is a mixture comprising from about 30 percent to 95 percent water-soluble salts of alkene disulfonates containing from about 10 to about 24 carbon atoms, and from about 5 percent to about 70 percent water-soluble salts of hydroxy disulfonates containing from about 10 to about 24 carbon atoms, said alkene disulfonates containing a sulfonate group attached to a terminal carbon atom and a second sulfonate group attached to an internal carbon atom not more than about six carbon atoms removed from said terminal carbon atom, the alkene double bond being distributed between the terminal carbon atom and about the seventh carbon atom, said hydroxy disulfonates being saturated aliphatic

compounds having a sulfonate radical attached to a terminal carbon, a second sulfonate group attached to an internal carbon atom not more than about six carbon atoms removed from said terminal carbon atom, and a hydroxy group attached to a carbon atom which is not more than about four carbon atoms removed from the site of attachment of said second sulfonate group.

The enzymes suitable for being incorporated into the inventive compositions can be of any origin, although they are mostly of animal and vegetable and particularly of bacterial origin. The enzyme preparations considered are mostly constituted by a mixture of different active substances all of which are characterized by a very specific enzymatic activity. They can be classified according to their activity. Examples of such sub-classes of enzymes are proteases, carbohydrases, esterases, oxido-reductases, catalysases, peroxydases, ureases, demolases, isomerases, nucleases and so on. As referred to hereinbefore, commercial enzyme preparations are seldom pure but constitute a mixture of different types of enzymes. Preferred for use in the detergent compositions of this invention are proteolytic enzyme preparations. A preferred enzyme component is a proteolytic enzyme, a serine protease. It is commercially available under the tradename of "ALCALASE" and manufactured by Novo Industri A/S, Copenhagen, Denmark. Other enzyme preparations being almost identical to ALCALASE for use in the detergent compositions of this invention are:

proteolytic enzyme derived from the genus *Bacillus*; this component is described in U.S. Pat. application Ser. No. 761,546, filed on Sept. 23, 1968, and has been deposited under the number 10 147 with The National Collection of Industrial Bacteria, Torry Research Station, Aberdeen Scotland.

protease mixture derived from *Bacillus subtilis* as sold by KALICHEMIE, Germany.

Takeda Fungal Alkaline Protease; Takeda Chemical Industries Ltd. Osaka, Japan.

The enzyme is to be used in a quantity of from about 0.005 percent to about 5 percent by weight of the composition. A preferred range includes a quantity of from about 0.1 percent to about 1.5 percent by weight of the enzyme preparation. Several non-proteolytic enzyme components can be mixed in wide ranges with the proteases species for use in the preferred embodiments of this invention. So for example, amylolytic enzyme preparations can advantageously be added. "AMYLAISE THC-250" manufactured by Rapidase, Seclin, France, represents an example of an amylolytic enzyme suitable for being used.

In addition to the essential ingredients listed hereinbefore, the inventive compositions can contain usual amounts of other ingredients and/or minor additives, all having well-defined functions in detergent technology and all being frequently present in the type of detergent compositions claimed. So, these compositions can contain solubilizing compounds which contribute in maintaining a uniform liquid detergent composition even during prolonged storage. From zero to 20 percent of the solubilizing compounds are usually incorporated into liquid detergent compositions. Typical examples suitable for the compositions claimed are the sodium salts of benzene sulfonate, toluene sulfonate, and xylene sulfonate. Lower alcohols can also satisfactorily be used, preferably those having from one through five carbon atoms.

Alkaline detergent builders can be employed in the compositions of this invention. In the event such builders are employed, their quantity does not normally exceed 20 percent because of the phase-stability problem which might flow from the use of higher quantities. Specific examples of inorganic builders suitable for use herein are alkali metal carbonates, phosphates, polyphosphates and silicates. The potassium and sodium salts of these builders are, for solubility reasons, the most suitable ones. Useful alkaline organic builders include the polyphosphonates, poly-acetates and polycarboxylates. Examples of polyphosphonates include the sodium and potas-

sium salts of ethylene diphosphonic acid, ethane-1-hydroxy-1,1-diphosphonic acid and ethane-1,1,2-triphosphonic acid. Polyacetate builders useful herein include the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetra-acetic acid; N-(2-hydroxyethyl)-ethylene diamine triacetic acid; N-(2-hydroxyethyl)-nitrilo diacetic acid; diethylenetriamine; and pentacetic acid. Water-soluble salts of polycarboxylate builders can also be used in these compositions. They are described in more detail in U.S. Pat. No. 3,308,067.

Enzyme-stabilizing agents in a quantity from 0 to 5 percent can also be used in the liquid detergent compositions of this invention. They have been found to be quite useful as they tend to improve the performance and particularly the storage stability advantages obtainable from the liquid detergent compositions claimed. Water-soluble calcium and magnesium chlorides, lactates and acetates represent the preferred stabilizing agents.

In addition, the liquid detergent compositions of the present invention can also contain other usual detergents additives not specifically referred to hereinbefore. For example, perfumes, anti-tarnishing agents, anti-redispersion agents, bacteriostatic agents, dyes, optical brighteners, fluorescers, suds depressors, suds boosters and the like can all be utilized herein without detracting from the advantageous stability and performance properties of the compositions of this invention.

The following Examples are illustrative of, but not limitative of, the claimed invention.

TEST METHOD

The performance advantages of the enzyme-containing detergent compositions of the invention are apparent from their use in the decomposition of standardized amounts of soil. In more detail, egg-soiled microscopic slides are immersed in a water-diluted solution of the test detergent composition. This detergent solution is then stirred and kept at 50° C by the aid of a heater-stirrer. The egg-soil testing slides are prepared by dipping microscopic slides into an intimately mixed yolk and egg-white. Then the slides are dried during 45 minutes at 50° C and cooked for half an hour at 105° C. The enzymatic activity is expressed as the average time required for achieving 95 percent soil-removal (T_{95}). Day-to-day variation of testing results are minimized by carrying out a reference run with a solution containing standardized amounts of surface-actives and enzymes.

The enzymatic activity can advantageously be expressed as a "cleaning index" (CI) corresponding to the following definition:

$$\frac{T_{95} \text{ of reference solution}}{T_{95} \text{ of test solution}} \times 100 = CI$$

This cleaning index comes actually quite close to the real enzymatic activity in washing solution under current usage conditions and is not affected by uncontrollable day-to-day variations.

EXAMPLE I

The cleaning performance superiority of the compositions claimed is readily recognizable from the following testing results. These experiments have been carried out with a set of conditions as listed

washing solution prepared by city water at 20 grains/gallon hardness
washing solution pH: 8.5; temperature: 50° C
product concentration in solution: see table
enzyme concentration in washing solution: 25 ppm ALCALASE containing 1.5* *(Anson, Journ. Gen Physiol. 22, 79 (1939).) AU/g

Composition	A	B	C
	(reference)		
	% by weight		

linear C ₁₂ alkylbenzene sulfonate-sodium salt	19		
sulfated (ethoxy) ₃ coconut alcohol-sodium salt	19	20	20
coconut monoethanolamide	2		
alkane sulfonate-sodium salt (C ₁₅₋₁₆)		20	
olefinsulfonate-sodium salt (C ₁₅₋₁₆)			20

The CI's of the compositions listed are:

Product concentration in solution (% by weight)	A	B	C
0.10		110	
0.125			140
0.185			140
0.25	100	145	140
0.30			155
0.35		170	

These results show the performance advantages achievable by the use of enzymes in combination with the detergent combinations of this invention.

EXAMPLE II

The inventive performance advantages are brought into prominence by comparing the CI's (cleaning indexes) measured for various active systems.

The test conditions are as indicated in Example I except for what concerns the product concentration in solution which is 0.25 percent by weight.

Surfactant system	% by weight surfactant in finished product	CI
(a) linear C ₁₂ alkyl benzene-sulfonate-Na	20	
sulfated (ethoxy) ₃ -Coconut alcohol-Na	20	100
(b) alkanesulfonate-Na (C ₁₅₋₁₆)	20	
sulfated (ethoxy) ₃ -coconut alcohol-Na	20	300
(c) olefin sulfonate-Na (C ₁₅₋₁₆)	20	
sulfated (ethoxy) ₃ -coconut alcohol-Na	20	380
(d) linear C ₁₂ alkyl benzene sulfonate-Na	20	
sulfate-(ethoxy) ₁₂ coconut alcohol-Na	20	100
(e) olefin sulfonate-Na (C ₁₅₋₁₆)	20	
sulfated (ethoxy) ₁₂ coconut alcohol-Na	20	400
(f) alkanesulfonate-Na (C ₁₅₋₁₆)	20	
sulfated (ethoxy) ₃ -coconut alcohol-Na	20	
condensate of tallow alcohol with 11 moles of ethylene oxide	10	330
(g) linear C ₁₂ alkyl benzene sulfonate-Na	40	
condensate of tallow alcohol with 11 moles of ethylene oxide	10	100

The improvement in cleaning performances as expressed by the CI's for trails (b), (c), (e) and (f) appears to be significant and also was unforeseeable.

EXAMPLE III

Different enzyme preparations have successively been incorporated into a liquid detergent composition with the following detergent system.

alkanesulfonate-Na (C ₁₅₋₁₆)	20% by weight
sulfated (ethoxy) ₃ -coconut alcohol-Na	20% by weight

The test conditions and the reference sample composition are the same as for Example I.

Enzyme Preparation	Enzyme activity in AU/g	ppm enzyme in washing solution	CI
ALCALASE	1.5	25	145
Protease mixture derived from Bacillus	1.5	25	140

subtilis (KALI)*			
ALCALASE	1.5	12.5	90
MONSANTO DA-10	1.8	12.5	80
KALI	1.5	12.5	90

The CI values confirm that the active system is effective with different types of enzymes.

EXAMPLE IV/A

Liquid detergent compositions were used for comparative performance testing thereby maintaining the following conditions:

- washing solutions prepared with city water 20 grains/gallon hardness
- solution pH = 7.0
- temperature: 50° C
- finished product concentration in solution: 0.25 percent
- enzyme concentration in washing solution: 25 ppm AL-CALASE (1.5 AU/g)

Ingredients	% by weight in finished product	CI
(a) linear C ₁₂ alkyl benzene sulfonate-Na	20	
condensate of nonylphenol with 9 moles of ethylene oxide	10	100
(b) alkanesulfonate-Na (C ₁₅₋₁₆)	20	
condensate of nonylphenol with 9 moles of ethylene oxide	10	200

*as sold by KALI CHEMIE, Germany

EXAMPLE IV/B

same conditions as example IV/A above

Ingredients	% by weight in finished product	CI
(a) linear C ₁₂ alkyl benzene sulfonate-Na	20	
condensate of tallow alcohol with 25 moles of ethylene oxide	10	100
(b) alkanesulfonate-Na (C ₁₅₋₁₆)	20	
condensate of tallow alcohol with 25 moles of ethylene oxide	10	140

The unexpected retention of enzymatic activity in liquid detergent compositions under prolonged storage conditions is apparent from the following Example.

EXAMPLE V

Liquid detergent samples are stored during one week at 35° C. The enzymatic activity is determined before and after storage.

- Detergent compositions tested:
- active system: see below
- ethanol: 12 percent by weight
- enzyme preparation: 1 percent by weight ALCALASE (1.5 AU/g)
- pH of composition is within the range from 7.0 to 9.0
- water: balance to 100.

Active System	% by wt. actives in detergent	% of initial enzymatic activity remaining after test
(a) linear C ₁₂ alkyl benzene sulfonate Na salt	19	
sulfated (ethoxy) ₃ coconut alcohol-Na salt	19	
coconut monoethanolamide	2	25
(b) alkane sulfonate-Na salt (C ₁₅₋₁₆)		
sulfated (ethoxy) ₃ coconut alcohol-Na salt	19	
coconut monoethanolamide	2	50
(c) olefin sulfonate-Na salt (C ₁₅₋₁₆)	19	
sulfated (ethoxy) ₃ coconut alcohol-Na salt	19	
coconut monoethanolamide	2	50
(d) C ₁₂ linear alkyl benzene sulfonate-Na salt	20	
condensate of nonylphenol with 9 moles of ethylene oxide	10	
(e) alkane sulfonate-Na salt (C ₁₅₋₁₆)	20	

	condensate of nonylphenol with 9 moles of ethylene oxide	10	50
(f)	C ₁₂ linear alkyl benzene sulfonate-Na salt	20	
	condensate of tallow alcohol with 25 moles of ethylene oxide	10	30
(g)	alkane sulfonate-Na salt (C ₁₅₋₁₆)	20	5
	condensate of tallow alcohol with 25 moles of ethylene oxide	10	55

The superior stabilization of the active enzymes in (b), (c), (e) and (g) is related to the choice of the active system.

EXAMPLE VI

Liquid detergent compositions identical to those described in Example V, except that 0.5 percent by weight of Ca acetate is added, were used for comparative testing as indicated in Example V.

Active System	% by wt. actives in detergent	% of initial enzymatic activity retained after test
(a) linear alkylbenzenesulfonate Na-salt (C ₁₂)	19	
sulfated (ethoxy) ₃ coconut alcohol-Na salt	19	
coconut monoethanolamide	2	25
(b) alkane sulfonate-Na salt (C ₁₅₋₁₆)	19	
sulfated (ethoxy) ₃ coconut alcohol-Na salt	19	
coconut monoethanolamide	2	85

These results show the increase in the stabilizing effect attained with the addition of a calcium salt to a composition as claimed.

EXAMPLE VII/A

The unforeseeable enzymatic stability can be enhanced as already apparent from Example VI through the addition of calcium and/or magnesium salts to the composition claimed. The following data serve as a further illustration of this.

The active composition used corresponds to composition (b) of Example V containing ALCALASE as enzyme preparation.

pH liquid composition: 7.0

Stabilizer salt used in detergent at a level of 1.0 percent by weight.

storage temperature: 20° C.

Stabilizer Salt	% of initial enzymatic activity retained after 5 weeks
Without	90
Calcium acetate	95
Magnesium acetate	95

EXAMPLE VII/B

The experimental conditions are the same as in Example VII/A above except:

Storage temperature: 35° C.

Stabilizer Salt	% in enzymatic activity retained after 5 weeks
Without	25
Calcium chloride	50
Calcium acetate	75
Magnesium chloride	50
Magnesium acetate	55

The data show the stabilizing effect obtained from the inventive compositions through the addition of stabilizing salts. No effect is noticed, however, when these stabilizers salts are added to the compositions representing the state of the art.

EXAMPLE VIII

Liquid detergent compositions were stored during two months at 20° C. The enzymatic activity is determined before and after storage.

Detergent compositions tested:

Active system: see below

ethanol: 12 percent by weight

enzyme preparation: 1 percent by weight ALCALASE (1.5 AU/g)

pH of composition is within the range from 7.0 to 9.0

water: balance to 100

Active System	% by wt. actives in detergent	% of initial enzymatic activity retained
(a) Linear C ₁₂ alkylbenzenesulfonate Na salt	20	
Condensate of tallow alcohol with 25 moles of ethylene oxide	10	75
(b) Alkane sulfonate Na salt (C ₁₅₋₁₆)	20	
Condensate of tallow alcohol with 25 moles ethylene oxide	10	90
(c) Linear C ₁₂ alkylbenzenesulfonate Na salt	20	
Condensate of nonylphenol with 9 moles of ethylene oxide	10	75
(d) Alkane sulfonate Na salt (C ₁₅₋₁₆)	20	
Condensate of nonylphenol with 9 moles of ethylene oxide	10	90
(e) Alkane sulfonate Na salt (C ₁₅₋₁₆)	19	
Sulfated (ethoxy) ₃ coconut alcohol Na salt	19	
Coconut monoethanolamide	2	90

What is claimed is:

1. A liquid detergent composition consisting essentially of, by weight of the detergent composition, a mixture of:

a. from about 2 percent to about 35 percent of an alkane sulfonate, or an alpha-olefin sulfonate which consists of a mixture of from about 30 percent to about 70 percent of Component A, from about 20 percent to about 70 percent of Component B, and from about 2 percent to about 15 percent of Component C, wherein

1. said Component A is a mixture of double-bond positional isomers of water soluble salts of alkene-1-sulfonic acids containing from about 10 to about 24 carbon atoms, said mixture of positional isomers including about 10 percent to about 25 percent of an alpha-beta unsaturated isomer, about 30 percent to about 70 percent of a beta-gamma unsaturated isomer, about 5 percent to about 25 percent of a gamma-delta unsaturated isomer, and about 5 percent to about 10 percent of a delta-epsilon unsaturated isomer;

2. said Component B is a mixture of water soluble salts of bifunctionally-substituted sulfur-containing saturated aliphatic compounds, containing from about 10 to about 24 carbon atoms, the functional units being hydroxy and sulfonate radicals with the sulfonate radical always being on the terminal carbon and the hydroxyl radical being attached to a carbon atom at least two carbon atoms removed from the terminal carbon atom, at least 90 percent of the hydroxy radical substitutions being in the three, four, and five positions; and

3. said Component C is a mixture comprising from about 30 - 95 percent water soluble salts of alkene disulfonates containing from about 10 to about 24 carbon atoms, and from about 5 percent to about 70 percent water soluble salts of hydroxy disulfonates containing from about 10 to about 24 carbon atoms, said alkene disulfonates containing a sulfonate group attached to a terminal carbon atom and a second sulfonate group attached to an internal carbon atom not more than about six carbon atoms removed from said terminal carbon atom, the alkene double bond being distributed between the terminal carbon atom and about the seventh carbon atom, said hydroxy disulfonates being saturated aliphatic compounds having a sulfonate radical attached to a terminal carbon, a second sulfonate group attached to an internal carbon atom not more than about six carbon atoms removed from said terminal carbon atom, and a hydroxy group attached to a

carbon atom which is not more than about four carbon atoms removed from the site of attachment of said second sulfonate group or mixtures of said alkane sulfonate and said olefin sulfonate, said compounds having from about 10 to about 26 carbon atoms in the hydrocarbon chain;

(b) from about 2 percent to about 30 percent of a compound having the formula:



wherein A is alkyl of from eight to 30 carbon atoms or alkyl phenyl with from three to 22 carbon atoms in the alkyl chain; E is an alkyleneoxy radical selected from the group of ethyleneoxy and propyleneoxy; n is an integer from 1 - 30 and X is hydroxyl or sulfate;

(c) from about 0.001 percent to about 5.0 percent of a proteolytic enzyme, and the balance of the composition to 100 percent being

water.

2. The liquid detergent composition of claim 1 wherein component (a) is present in an amount from about 10 percent to about 25 percent and component (b) is present in an amount from about 5% to about 20 percent and wherein X is sulfate.

3. The liquid detergent composition of claim 2 wherein component (b) has from 10 to 16 carbon atoms in the alkyl chain.

10 4. The liquid detergent composition of claim 1 wherein the alkane sulfonate or alpha-olefin sulfonate has from 12 - 20 carbon atoms in the hydrocarbon chain.

15 5. The liquid detergent composition of claim 1 wherein the amount of proteolytic enzyme employed is from about 0.1 percent to about 2.0 percent.

6. The liquid detergent composition of claim 5 wherein the proteolytic enzyme is from *Bacillus subtilis*.

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