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3,634,266

LIQUID DETERGENT COMPOSITIONS CONTAINING AMYLOLYTIC ENZYMES

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12 Claims

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SUMMARY OF THE INVENTION

These and other objects of the present invention are achieved by the provision of liquid detergent compositions having amylolytic enzyme activity and comprising:

- (1) from 1% to 65% of a water-soluble organic synthetic detergent;
- (2) from 0.1% to 3% of an amylolytic enzyme;
- (3) from 0.01% to 3% with respect to calcium ion of a water-soluble enzyme-stabilizing calcium salt;
- (4) from 0.01% to 5% of an alkali metal thiosulfate; and
- (5) the balance water.

The present invention is based in part on the discovery that amylolytic enzyme-containing liquid detergent compositions as hereinbefore defined can be stabilized substantially against loss of amylolytic enzyme activity by the provision of a water-soluble calcium salt and an alkali metal thiosulfate.

The water-soluble organic synthetic detergent of the compositions of the invention can be anionic, nonionic, ampholytic, zwitterionic or a mixture of these classes of detergents. Examples of detergents which can be used in the enzymatic liquid detergent compositions of the invention include anionic, nonionic, ampholytic and zwitterionic compounds described more fully hereinafter as follows:

(a) Anionic detergent compositions which can be used in the compositions of this invention include both soap and non-soap detergent compounds. Examples of suitable soaps are the sodium, potassium, ammonium and alkylol-ammonium salts of higher fatty acids (C_{10} – C_{20}). Particularly useful are the sodium or potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. Examples of anionic organic non-soap detergent compounds are the water-soluble salts, alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the synthetic detergents which form a part of the compositions of the present invention are the sodium or potassium alkyl sulfates especially those obtained by sulfating the higher alcohols (C_8 – C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzenesulfonates, such as are described in U.S. Letters Pat. No. 2,220,009 and No. 2,477,383 in which the alkyl group contains from about 9 to about 15 carbon atoms; other examples of alkali metal alkyl-benzene sulfonates are those in which the alkyl radical is a straight chain aliphatic radical containing from about 10 to about 20 carbon atoms for instance, 2-phenyl-dodecanesulfonate and 3-phenyl-dodecanesulfonate; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkylphenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 to about 12 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a methyl tauride in which the fatty acids, for example, are derived from coconut oil; and others known in the

ABSTRACT OF THE DISCLOSURE

Liquid detergent compositions having enzymatic activity and containing a water-soluble organic synthetic detergent, a water-soluble calcium salt, sodium thiosulfate, and amylolytic enzymes and water are disclosed. The compositions, useful in the cleansing of textiles and hard surfaces, are stabilized substantially against loss of amylolytic enzyme activity during storage.

FIELD OF THE INVENTION

This invention relates to aqueous amylolytic enzyme-containing detergent compositions useful in the degradation of starchy materials and in the cleansing of textiles and hard surfaces. More particularly, it relates aqueous detergent compositions stabilized against loss of amylolytic activity.

The use of amylolytic enzymes in the alteration and/or degradation of starchy materials is known. For example, U.S. Pat. 2,607,359 (Aug. 19, 1962) describes compositions containing an amylolytic enzyme useful in facilitating the removal of porous materials such as wall papers, labels and casein-type pastes from surfaces to which the porous materials are held by a starch-containing adhesive. Similarly, Jaag in Seifen, Ole, Fette, Wachse 88, No. 24, pp. 789–793 (November 1962) and German Patent 14,296 (published Jan. 6, 1958) each describe the use of amylolytic enzymes in laundry formulations. These enzymes aid in the cleaning process by attacking starchy soils and stains found on soiled fabrics or hard surfaces and decomposing and/or altering them so as to render them more removable during cleaning.

Enzymatic materials are expensive and powerful materials which must be judiciously formulated and used. It has long been recognized that enzymes are sensitive to and inactivated by environmental conditions such as pH, temperature, the effect of bleaches, and oxidizing agents. One of the more severe environmental influences as far as enzyme stability is concerned is the exposure of enzymatic materials to the hydrolytic effects of water. These enzymes when employed in aqueous compositions are unstable and suffer appreciable destruction during long periods of storage as evidenced by substantial loss in starch-degrading and/or soil- and stain-removing efficacy. The loss in amylolytic activity is particularly severe under conditions of high temperature. Accordingly, there has been a need for amylolytic enzyme-containing compositions having improved amylolytic enzyme stability.

It is therefore an object of this invention to provide liquid detergent compositions having enzymatic activity.

It is another object of this invention to provide aqueous amylolytic enzyme-containing compositions stabilized substantially against loss of activity by the presence of enzyme stabilizing compounds.

Other objects of this invention will be obvious from consideration of the invention which is more fully described hereinafter.

art, a number being specifically set forth in U.S. Letters Pats. Nos. 2,486,921; 2,486,922 and 2,396,278.

(b) Nonionic synthetic detergents may be broadly defined as compounds aliphatic or alkylaromatic in nature which do not ionize in water solution. For example, a well known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility has a molecular weight of from about 1,500 to 1,800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(1) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, or nonene, for example.

(2) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said hydrophobic base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

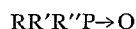
(3) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(4) Long chain tertiary amine oxides corresponding to the following general formula



wherein R_1 is an alkyl radical of from about 8 to 18 carbon atoms, and R_2 and R_3 are each methyl or ethyl radicals. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethyldecylamine oxide, dimethyltetradecylamine oxide, dinethylhexadecylamine oxide.

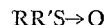
(5) Long chain tertiary phosphine oxides corresponding to the following formula



wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 18 carbon atoms in chain length and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphine oxides are: dinethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyldodecylphosphine oxide, ethylmethyldodecylphosphine oxide, dimethylstearylphosphine oxide, ethylethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, bis(hydroxyethyl)dodecylphosphine oxide, bis(2-hydroxyethyl)

dodecylphosphine oxide, 2-hydroxypropylmethyltetradecylphosphine oxide, dimethylolelphosphine oxide, and dimethyl-2-hydroxydodecylphosphine oxide.

(6) Dialkyl sulfoxides corresponding to the following formula



wherein R is an alkyl, alkenyl, beta or gamma-monohydroxyalkyl radical or an alkyl or beta- or gamma-monohydroxyalkyl radical containing one or two other oxygen atoms in the chain, the R groups ranging from 10 to 18 carbon atoms in chain length, and wherein R' is methyl or ethyl. Examples of suitable sulfoxide compounds are: dodecyl methyl sulfoxide, tetradecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 2-hydroxydodecyl methyl sulfoxide, 3-hydroxy-4-decoxybutyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide, 2-hydroxy-3-decoxypropyl methyl sulfoxide, 2-hydroxy-3-dodecoxypropyl methyl sulfoxide, dodecyl ethyl sulfoxide, and 2-hydroxy-dodecyl ethyl sulfoxide. The 3-hydroxy-4-decoxybutyl methyl sulfoxide is an especially effective detergent surfactant.

(c) Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group. Examples of compounds falling within this definition are sodium-3-dodecylaminopropionate and sodium-3-dodecylaminopropanesulfonate.

(d) Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium compounds in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contain an anionic water-solubilizing group. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate which are especially preferred for their excellent cool water detergency characteristics.

The anionic, nonionic, ampholytic and zwitterionic detergent surfactants mentioned above can be used singly or in combination in the practice of the present invention. The above examples are merely specific illustrations of the numerous detergents which can find application within the scope of this invention.

The amylolytic enzymes, which provide the liquid detergent compositions of the invention with amylolytic activity over a prolonged period of time, are known materials and can be of fungal, plant, animal or bacterial origin. Suitable amylolytic enzymes include the α -amylases which are particularly well suited for breaking down starch molecules by attacking the $\alpha_{1,4}$ -glycosidic linkages in starchy soils and stains. The resulting degraded short chains are then more easily removed from their environment with water or aqueous solutions of detergent. Examples of suitable amylolytic enzymes include the α -amylases of mold origin including those derived from *Aspergillus oryzae*, *Aspergillus niger*, *Aspergillus alliaceus*, *Aspergillus wentii*, and *Penicillium glaucum*. The α -amylases derived from cereal grains, pancreatic sources and such bacteria as *Bacillus subtilis*, *Bacillus macerans*, *Bacillus mesentericus* and *Bacillus thermophilus* are also useful herein. These enzymes are active in the pH range of from about 4.5 to about 10 and at temperatures from about 30° F. to about 150° F. Optimum activity of these α -amylases is generally exhibited in the pH range of from about 5.5 to about 7.5.

Preferred amylolytic enzymes herein are the α -amylases from the bacterial organism *Bacillus subtilis*. These amylases have high enzymatic activity and provide excellent starch-digestive properties which are especially useful in the laundering of textile materials containing soils

and stains of a starchy nature and in the washing of hard surfaces, e.g. dishes, pot and pans, having particles of starchy origin. These enzymes are also preferred for their ready availability and their degree of inherent resistance to detergent inactivation in detergent compositions.

The amylolytic enzymes useful herein can be employed in a pure state. Generally they are employed in the form of a powdered commercially available preparation wherein the amylolytic enzyme is present in an amount of from 2% to 80% of the preparation. The remaining portion, i.e., from 20% to 98%, comprises inert powdered materials. These powdered materials can comprise inorganic alkali metal salts such as sodium sulfate, sodium chloride, potassium silicate, sodium phosphate, inorganic alkaline earth metal salts such as calcium sulfate, magnesium sulfate, magnesium phosphate and the like; organic components such as non-enzymatic proteins, carbohydrates, organic clays, starches, lipids, color bodies and the like.

The amount of amylolytic enzyme employed in the compositions of this invention can vary depending upon the activity of the enzyme or enzyme preparation, conditions of pH and the intended use of the composition. The stabilized liquid detergent compositions of the invention contain an amount of amylolytic enzyme sufficient to provide efficient starch-degrading properties so as to facilitate the removal of soils and stains from laundered textile materials and to aid the cleaning of soiled dishware. The enzyme-containing detergent compositions of the present invention contain from 0.01% to 3% by weight α -amylase (calculated on the basis of pure α -amylase) and provide the requisite starch-degrading properties. These compositions contain from about 60 to 400,000 amylase activity units per gram of detergent composition. A preferred amount of α -amylase is from 0.025% to 0.075%. The precise amount of amylase employed can be readily determined by methods known in the art so long as the compositions of the invention have the hereinbefore described starch-degrading properties.

As used herein, amylolytic activity refers to the tendency of an amylolytic enzyme to perform the desired function of catalytic alteration and/or degradation of starchy materials. Stability or stabilization, as used herein, refers to the preservation of initial amylolytic enzyme activity. Stabilization against loss of initial enzymatic activity, as described herein, is in contrast to activation, the latter term referring to the employment of activating agents with weakly active or inactive enzymes to provide enzymatic activity.

The activity level of amylolytic enzymes suitable herein can be determined by numerous methods. A suitable method is the 3,5-dinitrosalicylate assay method. In accordance with this method, a sample of amylase is allowed to catalyze the hydrolysis of the 1,4- α -glycosidic bonds of starch and glycogens for five minutes at a temperature of 37° C. at a pH of 6.0. The reaction is terminated by the addition of buffered sodium 3,5-dinitrosalicylate, the color is developed and the amount of maltose determined by spectrophotometric response and comparison with solutions of analytical grade maltose hydrate. The amylase has one activity unit for each 0.4 mg. of maltose hydrate produced during hydrolysis under the specified conditions. The amylase activity method is well known and is described with particularity in P. Bernfeld, *Methods in Enzymol.* vol. I, p. 149 (1955).

Examples of commercial enzyme preparations suitable for use herein and the manufacturers thereof include: Diasmen α -amylase (Daiwa Kasei KK, Tokyo, Japan); Rapidase α -amylase THC-25 (Rapidase, Seclin, France); Novo Bacterial α -amylase (Novo Industri, Copenhagen, Denmark); Wallerstein α -amylase, Lot #454A (Wallerstein Company, Staten Island, N.Y.); Rhozyme-33 and Rohozyme H-39 (Rohm & Haas, Philadelphia, Pa.); α -Amylase (Miles Chemical Company, Elkhart, Ind.); the α -amylase which is an integral part of CRD-Protease (Monsanto DA-10) derived from *Bacillus subtilis* (Mon-

santo Company, St. Louis, Mo.); α -amylase (Midwest Biochemical Company, Milwaukee, Wis.); Maxatase and Maxamyl (Koninklijke Nederlandsche Gist-En Spiritusfabriek N.V., Delft, Netherlands). Mixtures of these materials can be employed in the compositions of the invention.

As hereinbefore described, the present invention is based in part upon the surprising discovery that extended periods of enzyme stabilization can be achieved by incorporating into aqueous enzyme solutions a combination of water-soluble calcium salt and alkali metal thiosulfate. The water-soluble salts of calcium include, for example, calcium chloride, calcium acetate, calcium citrate, calcium glycerol phosphate, calcium gluconate, calcium glucoheptanate, calcium lactate, calcium levulinate, calcium lactobionate, calcium malate, calcium lactophosphate, calcium succinate, and calcium maleate. The stabilized compositions of the invention are prepared to contain from 0.01% to 3% of the stabilized composition with respect to the calcium ion. Preferably from 0.25% to 1.5%, with respect to the calcium ion, is employed for best stabilization, particularly at elevated temperatures. Preferred calcium salts include calcium acetate which is readily available and provides excellent amylase stabilization.

The alkali metal thiosulfates which in concert with calcium salts provide desirable levels of amylolytic enzyme stabilization include sodium thiosulfate, potassium thiosulfate, and the like. Preferred herein is sodium thiosulfate which provides desirable levels of enzyme stabilization. The alkali metal thiosulfate of the present invention is employed herein in an amount of from 0.01% to 5% of the liquid detergent compositions. In a preferred embodiment of the present invention, the liquid detergent compositions comprise from 15% to 50% organic synthetic detergent; from 1% to 6% calcium acetate; from 0.02% to 3% sodium thiosulfate; from 0.025% to 0.075% of amylolytic enzyme and the balance water.

While the mechanism by which the calcium salts and alkali metal thiosulfates coact to protect amylolytic enzymes against loss of activity is not precisely known, the combination of salt and alkali metal thiosulfate provides levels of enzyme stability substantially greater than can be achieved by calcium stabilization alone. These levels of enzyme stability are in marked contrast to the rapid loss of activity which normally occurs by the severe hydrolytic influences of aqueous detergent compositions.

The water-soluble organic synthetic detergent can comprise a single detergent or a mixture of such detergents. In this respect, a preferred embodiment of the present invention is a liquid detergent composition which comprises from 11% to 37% of an alkali metal or ammonium alkyl sulfate having the formula $RO(C_2H_4O)_xSO_3M$ wherein R is alkyl of from 12 to 18 carbon atoms, x is from 0 to 10 and M is alkali metal or ammonium; from 2% to 6% of an alkali metal alkyl glyceryl ether sulfonate, the alkyl group containing from 10 to 18 carbon atoms; from 2% to 8% of a 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate, the alkyl having from 8 to 22 carbon atoms; from 1% to 6% calcium acetate; from 0.02% to 3% sodium thiosulfate; from 0.025% to 0.075% α -amylase; and the balance water.

These preferred compositions combine excellent cleaning and sudsing qualities, desirable starch-degrading properties and are particularly suited for light-duty fabric laundering and as dishwashing compositions. Especially preferred detergents are the 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonates which provide desirable cleaning effects and have desirable enzyme compatibility properties.

The stabilized aqueous compositions of this invention can also contain any of the usual detergent adjuvants, diluents and additives so long as they do not substantially interfere with the activity of the enzymatic components. For example, solubilizing agents such as ethanol, viscosity control agents such as toluene sulfonates and

xylene sulfonates, perfumes, anti-tarnishing agents, opacifiers such as ethylene glycol distearate or polystyrene, inert salts such as sodium sulfate, anti-redeposition agents, bacteriostic agents, dyes, fluorescers, suds builders, suds depressors, and the like, can be utilized herein without detracting from the advantageous properties of these compositions. It is preferred that the compositions of the present invention contain in addition certain proteolytic enzymes. These enzymes include the alkaline proteases, neutral proteases, and acid proteases which aid materially the removal of proteinaceous soils and stains from laun-

dered textiles. The employment of proteolytic enzymes in combination with the amylolytic enzymes of the present invention is preferred from the standpoint of facilitating the removal of a broad spectrum of varied soils and stains. The preferred proteolytic enzymes are the subtilisins, obtained from the bacterial organism, *Bacillus subtilis*. The improved stability characteristics of the enzyme-containing liquid detergent compositions of the invention are apparent from the following examples which serve to illustrate the invention and are not intended to restrict the invention. All parts set forth herein are by weight unless otherwise indicated.

TABLE 1

Composition	Stabilizing agent	Percent remaining activity after storage at 80° F. for—(weeks)			Percent remaining activity after storage at 90° F. for—(weeks)						Percent remaining activity after storage at 100° F. for—(weeks)		
		4	8	10	1	3	4	6	8	10	4	8	10
A	None	5			5	7	7	5			5		
B	2% calcium acetate	78			83	66	57	36			55		
C	4% calcium acetate	72			96	56	45	32			49		
D	2% calcium acetate plus 1% sodium thiosulfate	90	72	95	99	85	96	120	88	87	89	67	82
E	4% calcium acetate plus 1% sodium thiosulfate	92	77	104	108	91	96	114	69	84	93	67	102

The data presented in Table 1 shows the substantial amylase stability characteristics of the compositions of the present invention, i.e., Compositions D and E. The enhanced stability is in marked contrast to the loss in amylolytic activity which occurs when no stabilizing agent (Composition A) or when calcium ion (Compositions B and C) is employed.

EXAMPLE II

Liquid detergent compositions were prepared from the following components in the stated proportions.

EXAMPLE I

Liquid detergent compositions, A-E, were prepared from the following components in the stated proportions.

Composition	Parts by weights				
	A	B	C	D	E
Components:					
Ammonium salt of the sulfated condensation product of 1 mole of middle-cut coconut alcohol containing 2% C ₁₀ , 66% C ₁₂ , 23% C ₁₄ , and 9% C ₁₆ alkyl groups with 3 moles of ethylene oxide	25	25	25	25	25
Sodium alkyl glyceryl ether sulfonate having a long alkyl chain derived from the same middle-cut coconut alcohol	4	4	4	4	4
3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate wherein the alkyl group is derived from the same middle-cut coconut alcohol	5	5	5	5	5
Ethanol	7	7	7	7	7
Potassium toluene sulfonate	0.5	0.5	0.5	0.5	0.5
Ethylene glycol distearate	1	1	1	1	1
Miscellaneous (brightener, perfume, etc.)	6	6	6	6	6
Wallerstein α-amylase, Lot #454A (α-amylase from <i>Bacillus subtilis</i>)	0.5	0.5	0.5	0.5	0.5
Calcium acetate monohydrate		2	4	2	4
Sodium thiosulfate				1	1
Water	Balance to 100				

The liquid detergent compositions were stored in closed glass bottles for the times and temperatures indicated in Table 1. Each composition contained 0.5 part of Wallerstein α-amylase, Lot #454A (a commercially available enzyme preparation having about 180,000 amylase units per gram) corresponding to about 0.05% α-amylase on a pure basis. The amylolytic activity of each composition was measured at the stated intervals by the assay method hereinbefore described. In Composition A, no stabilizing agent was added. In Composition B, 2%

Composition	Parts by weight	
	F	G
Components:		
Ammonium salt of the sulfated condensation product of 1 mole of middle-cut coconut alcohol containing 2% C ₁₀ , 66% C ₁₂ , 23% C ₁₄ , and 9% C ₁₆ alkyl groups with 3 moles of ethylene oxide	25	25
Alkyldimethyl amine oxide wherein the alkyl is middlecut coconut alkyl	5	5
Sodium alkyl glyceryl ether sulfonate having a long alkyl chain derived from the same middle-cut coconut alcohol	4	4
Ethanol	7.2	7.2
Potassium toluene sulfonate	0.5	0.5
Miscellaneous (brightener, perfume, etc.)	6	6
Wallerstein α-amylase, Lot #454A (α-amylase from <i>Bacillus subtilis</i>)	0.5	0.5
Calcium acetate monohydrate	4	4
Sodium thiosulfate		0.5
Water	Balance to 100	

The compositions were stored in closed glass bottles for the times and temperatures indicated in Table 2 wherein the Percent Remaining Activity is tabulated:

TABLE 2

Composition	Recent Remaining Activity After Storage at 80° F. for—		Percent remaining activity after storage at 100° F. for—	
	2 weeks	4 weeks	2 weeks	4 weeks
F	3	10	7	19
G	104	95	112	116

The data presented in Table 2 shows the substantial amylase stability of Composition G of the invention, which is in marked contrast to that of Composition F employing calcium acetate monohydrate without the added presence of sodium thiosulfate.

EXAMPLE III

An effective, high-sudising, light-duty liquid detergent composition has the following components,

Components:	Parts by wt.
Ammonium salt of the sulfated condensation product of 1 mole of middle-cut coconut alcohol containing 2% C ₁₀ , 66% C ₁₂ , 23% C ₁₄ , and 9% C ₁₆ alkyl groups with 3 moles of ethylene oxide	15
3 - (N,N - dimethyl - N-alkylammonio)-2-hydroxypropane-1-sulfonate wherein the alkyl group is derived from the same middle-cut coconut alcohol	5
Condensation product of 1 mole of middle-cut coconut alcohol containing 2% C ₁₀ , 66% C ₁₂ , 23% C ₁₄ and 9% C ₁₆ alkyl groups with 20 moles of ethylene oxide	5
Potassium toluene sulfonate	2
Eethyl alcohol	2
Potassium chloride	2
Ethylene glycol distearate	1
Citric acid	0.1
Perfume	0.15
Brightener	0.09
Calcium acetate monohydrate	4
Sodium thiosulfate	1
Wallerstein α -amylase, Lot #454A (α -amylase from <i>Bacillus subtilis</i>)	0.5
Water	Balance to 100

These composition provides excellent starch-degrading properties useful in light-duty fabric washing and in the washing of dishes, pots and pans, kitchen utensils and other hard surfaces. The composition retains substantially its initial amylolytic activity.

Similar results are obtained when the following amylolytic enzymes are employed on an equal activity basis in lieu of the α -amylase employed in Example III in that light-duty liquid detergent compositions of efficient cleaning capacity and retained amylolytic activity are obtained: Diasmen α -amylase (Daiwa Kasei KK, Tokyo, Japan); Rapidase α -amylase THC-25 (Rapidase, Seclin, France); Novo Bacterial α -amylase (Novo Industri, Copenhagen, Denmark); Rhozyme-33 and Thozyme H-39 (Rohm & Haas, Philadelphia, Pa.).

Similar results can be obtained when the following water-soluble calcium salts, employed on an equivalent calcium ion basis, are employed in lieu of calcium acetate monohydrate, in that liquid detergent compositions of retained amylolytic activity are obtained: calcium chloride, calcium citrate, calcium glycerol phosphate, calcium gluconate, calcium glucoheptanate, calcium lactate, calcium levulinate, calcium lactobionate, calcium malate, calcium lactophosphate, calcium succinate and calcium maleate.

EXAMPLE IV

A liquid detergent composition having excellent cleansing properties and amylolytic activity for prolonged periods of time is prepared by admixing the following.

Components:	Parts by wt.
1-(coconut-alkyl dimethylammonio)-propane-3-sulfonate	3
Sodium alkyl benzene sulfonate wherein the alkyl group is a mixture of tri-, tetra- and penta-propylene and has an average carbon atom content of 12	9
Potassium pyrophosphate	20
Potassium toluene sulfonate	8
Ethanol	2
Sodium silicate solids (SiO ₂ /Na ₂ O is about 2.5)	3.6
Monsanto CRD-Protease (a commercially available mixture of proteases and amylases derived from <i>Bacillus subtilis</i> admixed with powdered vehicle)	0.5
Calcium acetate monohydrate	3
Potassium thiosulfate	1
Water	Balance to 100

Similar results can be obtained when the following organic detergents are employed in lieu of the 1-(coconut-alkyl dimethylammonio)-propane - 3 - sulfonate of Example IV: tallow alcohol ethoxylated with 11 moles of ethylene oxide; tallow alcohol ethoxylated with 30 moles of ethylene oxide; coconut alcohol ethoxylated with 6 moles of ethylene oxide; and 3-(N,N-dimethyl-N-coconut - alkylammonio)-2-hydroxypropane-1-sulfonate.

EXAMPLE V

A light-duty, liquid detergent composition having excellent sudsing and cleaning properties and amylolytic enzyme activity for prolonged periods of time contains the following components in parts by weight.

Components:	Parts by wt.
Ammonium salt of the sulfated condensation product of 1 mole of middle-cut coconut alcohol containing 2% C ₁₀ , 66% C ₁₂ , 23% C ₁₄ , and 9% C ₁₆ alkyl groups with 3 moles of ethylene oxide	15
Ammonium salt of linear alkyl sulfate wherein the alkyl is derived from the same middle-cut coconut alcohol	15
Alkyl monoethanolamide wherein the alkyl is a coconut-alkyl having 2% C ₁₀ , 66% C ₁₂ , 23% C ₁₄ and 9% C ₁₆ alkyl groups	4
Potassium xylene sulfonate	4
Ethanol	8
Miscellaneous (brightener, perfume, etc.)	5
α -Amylase from <i>Bacillus subtilis</i> (Wallerstein Lot #454A)	0.5
Monsanto CRD-Protease (a commercially available mixture of proteases and amylases derived from <i>Bacillus subtilis</i> admixed with powdered vehicle)	0.5
Calcium acetate monohydrate	5
Sodium thiosulfate	1
Water	Balance to 100

It is understood that the foregoing detailed description is given merely by way of illustration and that many variations can be made without departing from the spirit of the present invention.

Having described the invention, what is claimed is:

1. A liquid detergent composition stabilized against loss of enzymatic activity and consisting essentially by weight of the composition:

- (1) from 1% to 65% of a water-soluble organic synthetic detergent selected from the group consisting of anionic detergents, nonionic detergents, zwitterionic detergents, ampholytic detergents and mixtures thereof;
- (2) from 0.01% to 3% of an amylolytic enzyme;
- (3) from 0.01% to 3% with respect to calcium ion of a water soluble calcium salt;
- (4) from 0.01% to 5% of an alkali metal thiosulfate; and
- (5) the balance water.

2. The composition of claim 1 wherein the α -amylase is from *Bacillus subtilis*.

3. The composition of claim 2 wherein the amount of calcium ion is from 0.25% to 1.5%.

4. The composition of claim 3 wherein the amount of alkali metal thiosulfate is from 0.02% to 3%.

5. The composition of claim 4 wherein the water-soluble calcium salt is calcium acetate and the alkali metal thiosulfate is selected from sodium thiosulfate and potassium thiosulfate.

6. The composition of claim 1 wherein the water-soluble organic synthetic detergent is selected from the group consisting of anionic; nonionic; zwitterionic; ampholytic detergents; and mixtures thereof.

7. The composition of claim 6 wherein the water-

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soluble organic synthetic detergent comprises from 11% to 37% a detergent having the formula



wherein R is alkyl of from 12 to 18 carbon atoms, x is from 0 to 10 and M is alkali metal or ammonium; from 2% to 6% of an alkali metal alkyl glyceryl ether sulfonate wherein the alkyl group contains from 10 to 18 carbon atoms; and from 2% to 8% of a 3-(N,N-dimethyl-N - alkylammonio) - 2 - hydroxypropane - 1 - sulfonate wherein the alkyl has from 8 to 22 carbon atoms.

8. The composition of claim 7 wherein the amylolytic enzyme is an α -amylase from *Bacillus subtilis*.

9. The composition of claim 8 wherein the α -amylase is present in an amount of from 0.025% to 0.075%.

10. The composition of claim 9 wherein the calcium ion is present in an amount of from 0.25% to 1.5%.

11. The composition of claim 10 wherein the alkali metal thiosulfate is present in an amount of from 0.02% to 3%.

12. The composition of claim 11 wherein the water-soluble calcium salt is calcium acetate and the alkali metal thiosulfate is selected from sodium thiosulfate and potassium thiosulfate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,634,266 Dated January 11, 1972

Inventor(s) Kenneth W. Theile, David A. Lennert and Frederick G. Rose

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 41, after "and" insert -- East --.

Signed and sealed this 27th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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