

"STABILIZED BUILT LIQUID DETERGENT
COMPOSITION CONTAINING ENZYMES"

The present invention relates to stable, built, enzyme-containing liquid detergent compositions suitable for laundry or pre-soak formulations. More particularly, the present invention relates to

5. aqueous enzyme-containing liquid detergent compositions which contain one or more detergent builders and which are characterised by being physically stable, homogeneous liquid compositions.

The formulation of stabilized enzyme-containing

10. liquid detergent compositions has been the focus of much attention in the prior art. The desirability of incorporating enzymes into detergent compositions is primarily due to the effectiveness of proteolytic and amylolytic enzymes in decomposing proteinaceous and

15. starchy materials found on soiled fabrics, thereby facilitating the removal of stains, such as, gravy stains, blood stains, chocolate stains and the like during laundering. However, enzymatic materials suitable for laundry compositions, particularly

20. proteolytic enzymes, are relatively expensive. Indeed, they generally are among the most expensive ingredients in a typical commercial liquid detergent composition, even though they are present in relatively minor amounts. Moreover, enzymes are known to

25. be unstable in aqueous compositions. It is for this reason that an excess of enzymes is generally required in liquid detergent formulations to compensate for the expected loss of enzyme activity during prolonged periods of storage. Accordingly, the

30. prior art is replete with suggestions for stabilizing

enzyme-containing liquid detergent compositions, and in particular unbuilt liquid compositions by the use of various materials which are incorporated into the composition to function as enzyme stabilizers.

5. In the case of liquid detergent compositions containing a builder, the problem of enzyme instability is particularly acute. Primarily this is because detergent builders have a destabilizing effect on enzymes, even in compositions containing
10. enzyme stabilizers which are otherwise effective in unbuilt formulations. Moreover, the incorporation of a builder into a liquid detergent composition poses an additional problem, namely, the ability to form a stable single-phase composition; the solubility of
15. sodium tripolyphosphate, for example, being relatively limited in aqueous compositions, and especially in the presence of anionic and nonionic detergents.

- In U.K. Patent Application G.B. 2,079,305, published 20th January, 1982, there is disclosed an
20. aqueous built enzyme-containing liquid detergent composition which is stabilized by a mixture of a polyol and boric acid. As noted in the examples of the U.K. application, relatively large amounts of glycerol are required to stabilize the enzymes in the
25. composition. Yet, as demonstrated hereinafter in the present specification, the enzyme stabilizing effect provided by a mixture of glycerine and borax in a built aqueous liquid detergent composition is relatively modest.

30. In European Patent Application Publication No.

0126505, there is disclosed an aqueous enzyme-containing liquid detergent composition containing an enzyme stabilizing mixture consisting of certain dicarboxylic acids and borax. The dicarboxylic acids are recommended as a substitute for a polyol such as glycerol in known enzyme stabilizing mixtures consisting of glycerol and a boron compound. However, the dicarboxylic acid-borax mixtures of this publication in common with the aforementioned prior art mixture of glycerine and borax are incapable of providing anything other than a modest stabilizing effect in the present built liquid detergent compositions. Hence there is a need to markedly improve enzyme stability in aqueous built liquid detergent compositions of the type herein defined to levels far beyond the present capability of the compositions known in the art.

The present invention provides a stabilized built, enzyme-containing liquid detergent composition comprising:

(a) from 5 to 20%, by weight, of one or more surface active detergent compounds selected from the group consisting of anionic, nonionic and amphoteric detergent compounds;

(b) from 5 to 30%, by weight, of one or more builder salts selected from the group consisting of alkali metal tripolyphosphates, alkali metal carbonates, alkali metal nitrilotriacetates, and polyacetal carboxylates;

(c) an effective amount of an enzyme or an

enzyme mixture selected from the group consisting of alkaline protease enzymes and alpha-amylase enzymes;

(d) an enzyme-stabilizing system containing, based on the weight of the detergent composition, (i) from 1 to 10%, preferably 3 to 7%, glycerine; (ii) from 1 to 8%, preferably 1 to 5%, of a boron compound selected from the group consisting of boric acid, boric oxide and alkali metal borates and; (iii) from 0.5 to 8%, preferably 0.5 to 4%, of a carboxylic acid compound selected from the group consisting of mono, di and polycarboxylic acids having 1 to 8 carbon atoms and water-soluble salts thereof; and

(e) the balance comprising water and optionally perfume and other adjuvants.

In a preferred embodiment of the present invention, the liquid detergent composition comprises

(a) from 5 to 15% of an alkali metal alkyl-benzene sulphonate wherein the alkyl group contains 12 to 15 carbon atoms;

(b) from 2 to 5% of an alkali metal alkyl polyethoxy sulphate wherein the alkyl group contains 10 to 18 carbon atoms and the polyethoxy is of 3 to 11 ethylene oxide groups, the weight ratio of (a) to (b) being from about 2:1 to about 8:1;

(c) from 5 to 20% of sodium tripolyphosphate;

(d) from 1 to 10% of sodium carbonate, the weight ratio of (c) to (d) being from 2:1 to ~~about~~ 6:1;

(e) an effective amount of the aforesaid enzyme or enzyme mixture;

(f) an enzyme stabilizing system containing, based on the weight of the detergent composition, (i) from 3 to 7% glycerine, (ii) from 1 to 5% of an alkali metal borate and (iii) from 0.5 to 4% of the said carboxylic acid compound; and

(g) the balance comprising water and optionally perfume and other adjuvants.

The present invention also extends to a method of laundering comprising contacting the stained and/or soiled fabrics to be laundered with a stabilized enzyme-containing built liquid detergent composition in accordance with the present invention.

The described liquid detergent is a commercially acceptable heavy duty laundry detergent, capable of satisfactorily cleaning laundry items containing both oily and particulate soils. Additionally, the described compositions may be employed for the pre-treatment of badly soiled areas, such as collars and cuffs, of items to be laundered.

The present invention is predicated upon the discovery of a three component enzyme stabilizing system as herein defined which provides an enzyme stabilizing effect to the liquid detergent compositions of the present invention far in excess of that which can be achieved with conventional enzyme stabilizers. The enzyme stabilizing effect thus achieved reflects a synergy among the three components. In accordance with the present invention, the enzyme stability provided by a mixture of glycerine and borax or a mixture of borax and a

dicarboxylic acid as disclosed in the prior art can be synergistically improved by the use of the three component stabilizing system herein defined in the present liquid compositions so as to raise the level of enzyme stability significantly above that provided by either the mixture of glycerine and borax or the mixture of borax and dicarboxylic acid when used independently of each other as enzyme stabilizers. For commercial purposes, a desirable enzyme stability generally corresponds to about a half-life of one week at a temperature of 110°F (43°C).

The enzyme stabilizing system of the present invention is a mixture of glycerine, a boron compound selected from among boric acid, boric oxide and an alkali metal borate and a carboxylic acid compound as herein defined. The weight of the stabilizing system in the present built liquid detergent compositions is generally from about 3 to 25%, preferably about 6 to 15%, by weight. The weight ratio of glycerine to borax in the stabilizing mixtures is generally from about 1:1 to 3:1. The preferred amount of ~~glycerine~~^{boron compound} in the composition is from about 1 to 5%, and the preferred amount of carboxylic compound is from about 0.5 to 4% based on the weight of the composition.

The carboxylic acid compounds which are useful in the enzyme stabilizing system of the present invention encompass saturated as well as unsaturated mono, di and polycarboxylic acids having 1 to 8 carbon atoms among which are included oxalic acid (HOCCOOH), malonic acid ($\text{HOCCCH}_2\text{COOH}$), maleic acid

(HOOCCH:CHCOOH) and succinic acid ($\text{HOOCCH}_2\text{CH}_2\text{COOH}$). The carboxylic acids may contain hydroxy or amino substituents as exemplified by malic acid ($\text{HOOCCHOHCH}_2\text{COOH}$), tartaric acid (dihydroxysuccinic acid) aspartic acid (amino succinic acid) and citric acid. Preferred carboxylic acids of the present invention are succinic acid, maleic acid, malonic acid and malic acid and water soluble salts thereof. From a commercial standpoint, a particularly preferred carboxylic acid compound is citric acid and/or its salts because of their relatively low cost.

The alkaline proteolytic enzymes suitable for the compositions of the present invention include the various commercial liquid enzyme preparations which have been adapted for use in detergent compositions. Enzyme preparations in powdered form are also useful although, as a general rule, less convenient for incorporation into the built liquid detergent compositions. Thus, suitable liquid enzyme preparations include "Alcalase" (Registered Trade Mark) and "Esperase" (Registered Trade Mark) sold by Novo Industries, Copenhagen, Denmark, and "Maxatase" (Registered Trade Mark) and "AZ-Protease" sold by Gist-Brocades, Delft, The Netherlands.

Among the suitable α -amylase liquid enzyme preparations are those sold by Novo Industries and Gist-Brocades under the tradenames "Termamyl" (Registered Trade Mark) and "Maxamyl".

"Esperase" is particularly preferred for the present compositions because of its optimized activity at the higher pH values corresponding to the built detergent compositions.

The preferred detergents for use in the present liquid compositions are the synthetic anionic detergent compounds, and particularly a mixture of higher alkylbenzene sulphonate and alkyl polyethoxy

5. sulphate. While other water soluble higher alkylbenzene sulphonates may also be present in the formulas of the present invention, such as potassium salts and in some instances the ammonium or alkanol-ammonium salts, where appropriate, it has been found
10. that the sodium salt is highly preferred, which is also the case with respect to the alkyl polyethoxy sulphate detergent component. The alkylbenzene sulphonate is one wherein the higher alkyl group is of 12 to 15 carbon atoms, preferably 13 carbon
15. atoms. The alkyl polyethoxy sulphate, which also may be referred to as a sulphated polyethoxylated higher linear alcohol or the sulphated condensation product of a higher fatty alcohol and ethylene oxide or polyethoxylene glycol, is one wherein the alkyl group is
20. of 10 to 18 carbon atoms, preferably 12 to 15 carbon atoms, e.g. about 13 carbon atoms, and which includes 3 to 11 ethylene oxide groups, preferably 3 to 7, more preferably 3 to 5 and most preferably 3 or about 3 ethylene oxide groups. The ratio of alkylbenzene
25. sulphonate to polyethoxy sulphate in the detergent mixture is preferably from about 2:1 to 8:1 and most preferably from about 3:1 to 5:1, by weight. At ratios above 5:1, the physical stability of the product may be adversely affected.
30. In suitable circumstances other anionic deter-

- gents, such as fatty alcohol sulphates, paraffin sulphonates, olefin sulphonates, monoglyceride sulphates, sarcosinates and similarly functioning detergents, preferably as the alkali metal, e.g.
5. sodium salts, can be present, sometimes in partial replacement of the previously mentioned synthetic organic detergents but usually, if present, in addition to such detergents. Normally, the supplementing detergents will be sulphated or
 10. sulphonated products (usually as the sodium salts) and will contain long chain (8 to 20 carbon atoms) linear or fatty alkyl groups. In addition to any supplementing anionic synthetic organic detergents, there also may be present nonionic and amphoteric
 15. materials, like the Neodols (Registered Trade Mark), sold by Shell Chemical Company, which are condensation products of ethylene oxide and higher fatty alcohols, e.g. Neodol (Registered Trade Mark) 23-6.5, which is a condensation product of a higher fatty alcohol of
 20. about 12 to 13 carbon atoms with about 6.5 moles of ethylene oxide. Illustrations of the various detergents and classes of detergents mentioned may be found in the text Surface Active Agents, Vol. II, by Schwartz, Perry and Berch (Interscience Publishers,
 25. 1958), the descriptions of which are incorporated herein by reference.

The builder salt combination of the present invention, which has been found to satisfactorily improve the detergency of the mixture of synthetic

30. anionic organic detergents and produce the desired pH

- in the liquid detergent and in the wash water, is a mixture of sodium tripolyphosphate and sodium carbonate. The builder salts are employed in the compositions of the present invention in amounts
5. generally of from about 5 to 25%, by weight. For the preferred builder salt combination, sodium tripolyphosphate is present in amounts of from about 5 to 20%, preferably 10 to 16%, and sodium carbonate is present from about 1 to 10%, by weight, preferably 3
10. to 7%, the weight ratio of tripolyphosphate to carbonate in the preferred builder mixtures being from about 2:1 to 6:1, and most preferably from about 2:1 to 4:1. As used herein, the term alkali metal "carbonates" or "carbonate" is meant to include the
15. carbonates, bicarbonates and sesquicarbonates of such alkali metals.

- For best processing, easier mixing and good end-use properties it is preferred that the sodium tripolyphosphate be low in content of Phase I type tripolyphosphate. Thus, normally the content of Phase I
20. type tripolyphosphate will be less than 30% of the tripolyphosphate employed. Although in some instances incompletely neutralized tripolyphosphate may be used, normally the phosphate employed may be
25. considered as being pentasodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$. Of course, in some instances, as when potassium salts of other materials are present, ion interchange in an aqueous medium may result in other salts than the sodium tripolyphosphate being present
30. but for the purpose of this specification it will be

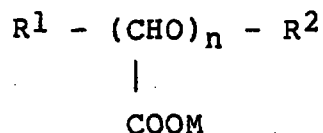
considered that sodium tripolyphosphate, as the pentasodium salt, the material which is normally charged to the mixer to make the present liquid detergent, is the tripolyphosphate employed.

5 Other preferred builder salts which may be used in place of sodium tripolyphosphate and sodium carbonate or in addition thereto include a polyacetal carboxylate as herein described and sodium nitrilotriacetate (NTA). Of course, various mixtures
10 of the mentioned water soluble builder salts can be utilized. Yet, the tripolyphosphate-carbonate mixture described has been found to be most preferred, although the other builders and mixtures thereof are also operative. Other builders which may
15 be employed as supplements, in addition to the proportions of the above-mentioned builders, include other phosphates, such as tetrasodium pyrophosphate or tetrapotassium pyrophosphate, sodium citrate, sodium gluconate and sodium silicate.

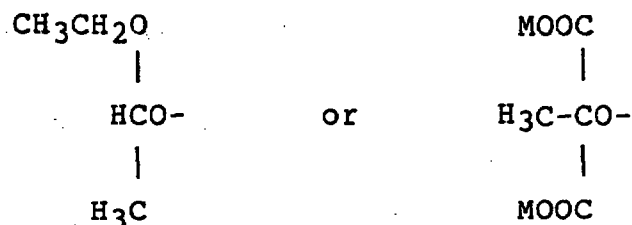
20 Polyacetal carboxylates are generally described in U.S. Patents 4,144,226 and 4,315,092. U.S. Patent 4,146,495 describes detergent compositions containing polyacetal carboxylates as builders.

25 The polyacetal carboxylates which are useful herein as builders may be considered to be those

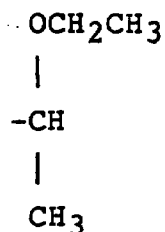
described in U.S. Patent 4,144,226 and may be made by the method mentioned therein. A typical such product will be of the formula



wherein M represents an alkali metal, or ammonium, or an alkyl group of 1 to 4 carbon atoms, or a tetra-alkylammonium group or an alkanolamine group, both of 1 to 4 carbon atoms in the alkyls thereof, n averages at least 4, and R¹ and R² represent any chemically stable group which stabilizes the polymer against rapid depolymerization in alkaline solution. Preferably the polyacetal carboxylate will be one wherein M is alkali metal, e.g. sodium, n is from 20 or 50 to 200, R¹ is



or a mixture thereof, R² is



and especially where n averages from 20 to 100, more preferably 30 to

80. The calculated weight average molecular weights of the polymers will normally be within the range of 2,000 to 20,000, preferably 3,500 to 10,000 and more preferably 5,000 to 9,000, e.g. about 8,000.

5 A particularly preferred sodium polyacetal carboxylate is supplied by Monsanto Company and is known as Builder U. It has a calculated weight average molecular weight of about 8,000 and an active polymer content of about 80%.

10 Although the preferred polyacetal carboxylates have been described above, it is to be understood that they may be wholly or partially replaced by other such polyacetal carboxylates. Also, the chain
15 terminating groups described in the various patents, especially U.S. 4,144,226, may be utilized, providing that they have the desired stabilizing properties, which allow the mentioned polyacetal carboxylate
20 builders to be depolymerized in acidic media, facilitating biodegradation thereof in waste streams, but maintain their stability in alkaline media, such as washing solutions.

 The only other required component of the liquid detergents of the present invention is water. Normally the hardness content of such water will be
25 less than about 300 ppm, as CaCO_3 , and preferably it will be less than 150 ppm. Often it may be desirable to utilize deionized water although city water with

less than 50 or 100 p.p.m. hardness content will frequently be equally satisfactory.

- Various adjuvants may be present in the liquid detergents of the present invention, such as fluorescent brighteners, perfumes and colourants. The fluorescent brighteners include the well known stilbene derivatives, including the cotton and nylon brighteners, such as those sold under the trademark Tinopal (5BM Conc.). The perfumes that are employed usually include essential oils, esters, aldehydes and/or alcohols, all of which are known in the perfumery art. The colourants may include dyes and water dispersible pigments of various types, including ultramarine blue. Inorganic filler salts, such as sodium sulphate and sodium chloride may be present, as may be antiredeposition agents, such as sodium carboxymethylcellulose; dispersing agents, such as sodium polyacrylate; bleaches; bactericides; fungicides; anti-foam agents, such as silicones; anti-soiling agents, such as copolyesters; preservatives such as formalin; foam stabilizers, such as lauric myristic diethanolamide; and auxiliary solvents, such as ethanol. Normally the individual proportions of such adjuvants will be less than 3%, often less than 1% and sometimes even less than 0.5%, except for any fillers and solvents, and additional detergents and builders for which the proportions may sometimes be as high as 10%. The total proportion of adjuvants, including non-designated synthetic detergents and builders, will normally be no more than 20% of the

- product and desirably will be less than 10% thereof, more desirably less than 5% thereof. Of course, the adjuvants employed will be selected so as not to interfere with the washing action of the liquid detergent and to avoid instability of the product on standing. Also, adjuvants which cause the production of objectionable deposits on the laundry are to be avoided.

- The liquid compositions of the present invention are efficient and easy to use. Compared to heavy duty laundry detergent powders, much smaller volumes of the liquids of the present invention are employed to obtain comparable cleaning of soiled laundry. For example, using a typical preferred formulation of the present invention, only about 132 grams or 1/2 cup of liquid is needed for a full tub of wash in a top-loading washing machine in which the water volume is 15 to 18 gallons (57 to 68 litres); and even less is needed for front-loading machines. Thus, the concentration of the liquid detergent composition in the wash water is of the order of about 0.2%. Usually, the amount of the liquid composition in the wash solution will range from about 0.05 to 0.3%, preferably from 0.15 to 0.25%. The proportions of the various constituents of the liquid composition may vary accordingly. Equivalent results can be obtained by using greater amounts of a more dilute formulation but the greater quantity needed will require additional packaging and will generally be less convenient for consumer use and may also result in product separation.

- The viscosity of the liquid detergent composition of the present invention is normally in the range of about 1000 to 10,000 centipoises, preferably 2000-5000 centipoises, but products of other suitable viscosities may also be useful. At the viscosities mentioned, the liquid detergent is pourable, stable, non-separating and uniform. The pH of the liquid detergent suspension usually in the range of 7 to 11.5, preferably 8 to 10.5, appears to help to maintain product stability and pourability.

- The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples. Unless otherwise indicated all parts are by weight and temperatures are in °C.

EXAMPLE 1

- A liquid detergent composition is made up with the ingredients and proportions shown in Table 1 below.

TABLE 1

<u>Component</u>	<u>Percent</u>
Pentasodium tripolyphosphate	15.0
Sodium carbonate	5.0
25. Sodium linear tridecylbenzene sulphonate	12.2
AEOS(1)	2.8
Carboxymethyl cellulose (CMC)	0.15
Optical brightener	0.4
Perfume	0.3
30. Enzyme (Esperase 8.OL)(2)	1.0

TABLE 1 (continued)

<u>Component</u>	<u>Percent</u>
Glycerine	4.0
Borax	3.0
5. Triethanolamine	1.0
Sodium citrate	2.0
Water and adjuvants	Balance

Notes on Table 1:

10. (1) Sodium alkyl polyethoxy sulphate wherein the alkyl group is of 12 to 15 carbon atoms and the polyethoxy is of 3 ethoxy groups.
15. (2) "Esperase" sold by Novo Industries having an activity of 8.0 KNPu/gram (Kilo Novo Protease units/gm).

The composition set out in Table 1 was prepared by the following procedure: 32.5 parts of deionized

20. water at 40°F (4°C) are added to a suitable mixing apparatus such as a vertical cylindrical tank equipped with a stirrer. With the stirrer adjusted for medium agitation, a mixture consisting of 5.0

25. parts anhydrous soda ash and 0.17 parts sodium carboxymethyl cellulose is incorporated into the water. The stirrer speed is then increased to maximum agitation and 15.0 parts pentasodium tri-

30. polyphosphate is slowly added to the mixing apparatus over a period of 10-15 minutes to form a milky white suspension. The agitation speed is then decreased to

- a slow/medium setting while 19.1 parts of a high AI (about 50%) LTBS (linear tridecylbenzene sulphonate) slurry is added. Thereafter the optical brightener/colour solution is added consisting of 0.4 parts
5. Tinopal LMS-X (CIBA-GEIGY), 0.06 parts blue dye and 2.0 parts deionized water. Once a uniform blue coloured solution is obtained, 0.3 parts of perfume are added to the mixture under agitation. This is followed by the slow addition of 4.0 parts glycerine,
10. 3.0 parts borax and 1.0 part triethanolamine (the TEA improves long term product stability) as a three component slurry. Stirring is continued until the mixture is uniform in appearance and then 2.0 parts of sodium citrate and 4.0 parts water are slowly
15. added. Agitation of the mixture is then reduced while a mixed AI detergent base consisting of 5.7 parts LTBS slurry (about 50% AI) and 4.7 parts AEOS (about 60% AI) is added to the mixture. This is followed by the slow addition of 1.0 part proteolytic
20. enzyme with continuous agitation until all materials are completely dispersed or dissolved.

EXAMPLES 2A to 2G

- Enzyme-containing built liquid detergent compositions, Examples 2A to 2G, were formulated as
25. set forth below in Table 2. The percentages shown indicate weight percent. It will be appreciated that the compositions are identical in respect of the first eight components listed in Table 2.

Examples 2A to 2F are comparison examples.

TABLE 2

<u>Component</u>		<u>2A</u>	<u>2B</u>	<u>2C</u>	<u>2D</u>	<u>2E</u>	<u>2F</u>	<u>2G</u>
Pentasodium tri- polyphosphate		15%	15%	15%	15%	15%	15%	15%
5.	Sodium Carbonate (anhydrous)	5	5	5	5	5	5	5
Sodium linear tri- decylbenzene sulphonate		12.2	12.2	12.2	12.2	12.2	12.2	12.2
10.	AEOS(1)	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Optical brightener (Tinopal LMS-X)		0.4	0.4	0.4	0.4	0.4	0.4	0.4
Perfume		0.3	0.3	0.3	0.3	0.3	0.3	0.3
CMC		0.2	0.2	0.2	0.2	0.2	0.2	0.2
15.	Enzyme(2)	1	1	1	1	1	1	1
Glycerine		-	4	-	4	-	-	4
Borax		-	-	3	3	-	3	3
Carboxylic acid compound		-	-	-	-	2	2	2
20.	Water and adjuvants	-----Balance-----						

Notes on Table 2:

- (1) Sodium alkyl polyethoxy sulphate wherein the
25. alkyl group is of 12 to 15 carbon atoms and the
polyethoxy is 3 of ethoxy groups.
- (2) "Esperase" sold by Novo Industries having an
activity of 8.0 KNPu/gm (Kilo Novo Protease
30. units/gm).

The enzyme activities of the compositions of Examples 2A to 2G were tested after 7 days storage at 110°F (43°C). The measured enzyme activity for each composition after this period of storage is indicated in Tables 3A to 3C and Table 4 as a percent of the initial value. Various components used in the formulas of the compositions of Examples 2A to 2G are shown in Tables 3A to 3C; those of Examples 2A to 2D are shown in Table 3A as well as the enzyme activities corresponding to each composition; those of Example 2E in Table 3B (these all being comparison examples) and those of Example 2G in Table 3C (this being in accordance with the invention).

TABLE 3A
ENZYME STABILITY

<u>Example</u>	<u>Composition</u>	<u>Percent Active Enzyme After 7 Days at 110°F (43°C)</u>
2A	(control)	ND*
2B	(with glycerine)	ND
2C	(with borax)	ND
2D	(with glycerine and borax)	45

TABLE 3B

Composition E (with carboxylic acid compound)
wherein the carboxylic acid compound is:

5.	<u>Example Composition</u>	<u>Percent Active Enzyme After 7 Days at 110°F (43°C)</u>
	2E (1) Sodium Succinate	ND*
	2E (2) Succinic acid	ND
	2E (3) Malonic acid	ND
10.	2E (4) Malic acid	ND
	2E (5) Oxalic acid	ND
	2E (6) Maleic acid	ND
	2E (7) Tartaric acid	ND
	2E (8) Aspartic acid	ND
15.	2E (9) Citric acid	ND
	2E (10) Glycine	ND
	2E (11) Alanine	ND
	2E (12) Sodium formate	ND
	2E (13) Sodium acetate	ND
20.	2E (14) Sodium tartrate	ND
	2E (15) Sodium citrate	ND
	2E (16) Sodium glycolate	ND
	2E (17) Sodium tetrahydroxysuccinate	ND

25. Note on Tables 3A and 3B

* ND = Not detectable (below 10% residual activity).

TABLE 3C

Composition G (with glycerine/borax/carboxylic acid compound) wherein the carboxylic acid compound is:

<u>Example Composition</u>		<u>Percent Active Enzyme After 7 Days at 110°F (43°C)</u>
5.	2G (1) Sodium succinate	60
	2G (2) Succinic acid	94
10.	2G (3) Malonic acid	91
	2G (4) Malic acid	79
	2G (5) Oxalic acid	81
	2G (6) Maleic acid	88
	2G (7) Tartaric acid	63
15.	2G (8) Aspartic acid	84
	2G (9) Citric acid	62
	2G (10) Glycine	80
	2G (11) Alanine	79
	2G (12) Sodium formate	57
20.	2G (13) Sodium acetate	50
	2G (14) Sodium tartrate	54
	2G (15) Sodium citrate	57
	2G (16) Sodium glycolate	50
	2G (17) Sodium tetrahydroxy succinate	61
25.		

As is evident from Table 3A, the control composition of Example 2A, as well as the comparison compositions of Examples 2B and 2C which contained glycerine and borax, respectively, as individual stabilizers, manifested almost no enzyme activity after the 7 day

30. manifested almost no enzyme activity after the 7 day

storage period of 110°F (43°C). Since enzyme activities below 10% could not be precisely measured they are designated "ND". The comparison composition of Example 2D containing glycerine and borax in the absence of a carboxylic acid compound provided an improvement in enzyme stability relative to the compositions of Examples 2A to 2C but more than 50% of the enzyme was deactivated. The various comparison compositions of Examples 2E(1) to 2E(17) containing a variety of carboxylic acid compounds but no borax or glycerine, as indicated, manifested absolutely no improvement in enzyme stability relative to the compositions of Examples 2A to 2C. However, the compositions of Examples 2G(1) to 2G(17) formulated in accordance with the invention (using the same carboxylic acid compounds) demonstrate the unexpected and synergistic improvement in enzyme stability which is achieved with the use of glycerine and borax in combination with a carboxylic acid compound in liquid detergent compositions as required by the present invention. It is noted that in every one of the compositions corresponding to Examples 2G(1) to 2G(17) which were tested, the enzyme activity was improved relative to the composition of Example 2D (containing only glycerine and borax).

A comparison of the enzyme activities achieved with the composition of Example 2D (glycerine and borax) and various compositions of Example 2F (borax and carboxylic acid compound) and of Example 2G (formulated in accordance with the invention) is set forth below in Table 4.

TABLE 4
ENZYME STABILITY

5	<u>Example Composition</u>	Percent Active Enzyme After 7 Days at 110°F (43°C)
	2D (Glycerine/borax)	45
	2F (1) (Borax/malonic acid)	13
	2G (3) (Glycerine/borax/malonic acid)	91
	2F (2) (Borax/aspartic acid)	39
10	2G (8) (Glycerine/borax/aspartic acid)	84
	2F (3) (Borax/citric acid)	ND*
	2G (9) (Glycerine/borax/citric acid)	62

Notes on Table 4

- 15 * ND - Not detectable (below 10% residual activity)
 2F(1) corresponds to 2G(3); 2F(2) corresponds to
 2G(8) and 2F(3) corresponds to 2G(9).

20 As shown in Table 4, the various compositions of
 Example 2G(3), 2G(8) and 2G(9) containing a three
 component stabilizer system in accordance with the
 present invention provided a synergistic improvement
 in enzyme stability relative to the compositions of
 Examples 2D and 2F(1), 2F(2) and 2F(3) formulated in
 25 accordance with the prior art.

CLAIMS

5 1. A stabilized enzyme-containing built liquid detergent composition comprising:

(a) from 5 to 20%, by weight, of one or more surface active detergent compounds selected from the group consisting of anionic, nonionic and amphoteric detergent compounds;

10 (b) from 5 to 30%, by weight, of one or more builder salts selected from the group consisting of alkali metal tripolyphosphates, alkali metal carbonates, alkali metal nitrilotriacetates and polyacetal carboxylates;

15 (c) an effective amount of an enzyme or an enzyme mixture selected from the group consisting of alkaline protease enzymes and alpha-amylase enzymes;

(d) an enzyme-stabilizing system containing, based on the weight of the detergent composition, (i) from 1% to 10% glycerine; (ii) from 1 to 8% of a boron compound selected from the group consisting of boric acid, boric oxide and alkali metal borates; and (iii) from 0.5 to 8% of a carboxylic acid compound selected from the group consisting of mono, di and polycarboxylic acids having 1 to 8 carbon atoms and water-soluble salts thereof; and

25 (e) the balance comprising water and optionally perfume and other adjuvants.

30 2. A liquid detergent composition as claimed in Claim 1 comprising:

(a) from 5 to 15% of an alkali metal alkyl-



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benzene sulphonate in which the alkyl group contains 12 to 15 carbon atoms;

(b) from 2 to 5% of an alkali metal alkyl polyethoxy sulphate in which the alkyl group contains 10 to 18 carbon atoms and the polyethoxy is of 3 to 11 ethylene oxide groups, the weight ratio of (a) to (b) being from ^{about}2:1 to ^{about}8:1;

(c) from 5 to 20% of sodium tripolyphosphate;

(d) from 1 to 10% of sodium carbonate, the weight ratio of (c) to (d) being from 2:1 to 6:1;

(e) an effective amount of the said enzyme or enzyme mixture;

(f) the enzyme stabilizing system containing, based on the weight of the detergent composition, (i) from 3 to 7% glycerine, (ii) from 1 to 5% of an alkali metal borate and (iii) from 0.5 to 4% of the said carboxylic acid compound; and

(g) the balance comprising water and optionally perfume and other adjuvants.

3. A liquid detergent composition as claimed in Claim 2 in which the said alkali metal alkylbenzene sulphonate is sodium linear tridecylbenzene sulphonate and the said alkali metal alkyl polyethoxy sulphate is one in which the alkali metal is sodium, the alkyl group contains 12 to 15 carbon atoms and the polyethoxy is of about 3 ethylene oxide groups.



4. A liquid detergent composition as claimed in Claim 2 or Claim 3 in which the ratio of alkylbenzene sulphonate to polyethoxy sulphate is from 3:1 to 5:1.

5. A liquid detergent composition as claimed in any one of Claims 1 to 4 in which the said boron compound is an alkali metal borate.

6. A liquid detergent composition as claimed in Claim 5 in which the said borate is borax.

7. A liquid detergent composition as claimed in any one of Claims 2 to 6 which contains from 10 to 16% sodium tripolyphosphate and from 3 to 7% sodium carbonate.

8. A liquid detergent composition as claimed in any one of Claims 1 to 7 in which the said carboxylic acid compound is succinic acid or a water-soluble salt thereof.

9. A liquid detergent composition as claimed in any one of Claims 1 to 7 in which the said carboxylic acid compound is maleic acid or a water-soluble salt thereof.

10. A liquid detergent composition as claimed in any one of Claims 1 to 7 in which the said carboxylic acid compound is citric acid or a water-soluble salt thereof.



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11. A liquid detergent composition as claimed in any one of Claims 1 to 7 in which the said carboxylic acid compound is malonic acid or a water-soluble salt thereof.

12. A liquid detergent composition as claimed in any one of Claims 1 to 7 in which the said carboxylic acid compound is malic acid or a water-soluble salt thereof.

13. A liquid detergent composition as claimed in Claim 1 substantially as specifically described herein with reference to any one of Example 1 or Examples 2G(1) to 2G(17).

14. A method of laundering comprising contacting the stained and/or soiled fabrics to be laundered with a stabilized enzyme-containing built liquid detergent composition as claimed in any one of Claims 1 to 13.

