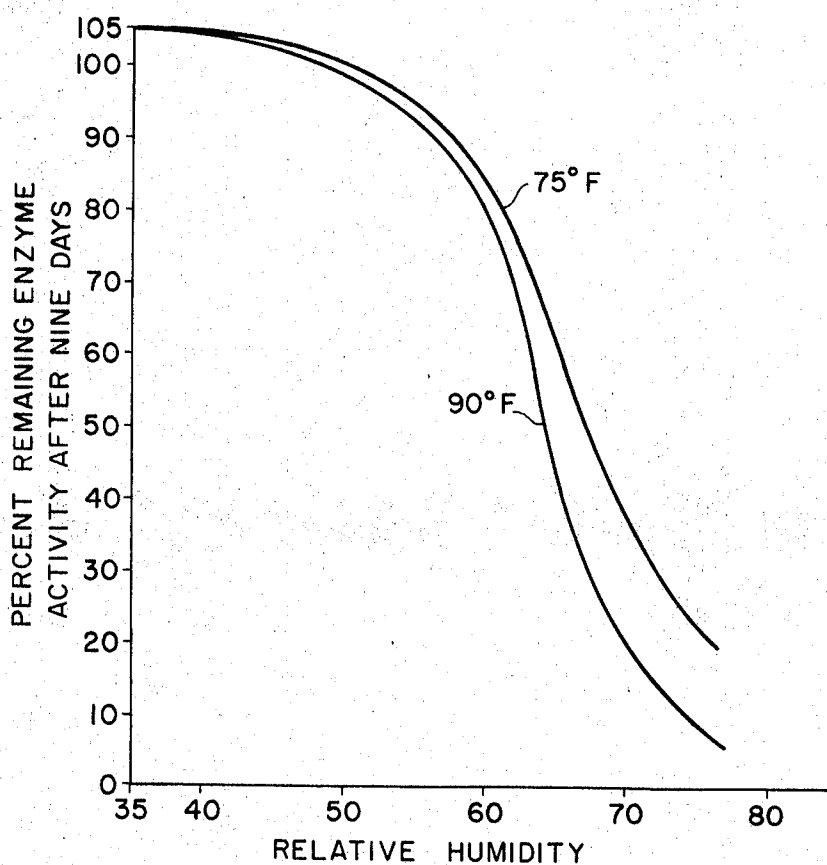


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JEAN-PIERRE D. B. EYMERY ET AL
GRANULAR DETERGENT COMPOSITION CONTAINING ENZYMES
AND ENVIRONMENTAL CONTROL COMPONENTS
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INVENTORS

Jean-Pierre D. B. Eymery
Harold H. Beyer

BY

Michael D. Ellerton

ATTORNEYS

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GRANULAR DETERGENT COMPOSITION CONTAINING ENZYMES AND ENVIRONMENTAL CONTROL COMPONENTS

Jean-Pierre D. B. Eymery and Harold H. Beyer, Springfield Township, Hamilton County, Ohio, assignors to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

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8 Claims

ABSTRACT OF THE DISCLOSURE

Granular detergent composition containing enzymes and environmental control components wherein the environmental control components are selected from the group consisting of sodium perborate trihydrate, anhydrous trisodium phosphate, anhydrous calcium sulfate and mixture thereof; and soluble or dispersible proteins having a molecular weight of between about 5,000 and 1,000,000 in an effective amount to stabilize the enzymes in the granular detergent composition in combination with a component selected from the group consisting of sodium perborate trihydrate, anhydrous trisodium phosphate, anhydrous calcium sulfate and mixtures thereof.

FIELD OF THE INVENTION

The present invention relates to a granular detergent composition containing enzymes and environmental control components. The environmental control components utilized herein inhibit oxidation and/or autolysis of enzymes by controlling the relative humidity in the packaged granular, enzyme-containing detergent composition and, in one embodiment, by complexing the enzymes with proteins in conjunction with controlling the relative humidity in the packaged granular detergent composition.

HISTORY OF THE INVENTION

The use of enzymes in admixture with detergent compositions is quite old. See Ferlinghusen, U.S. Pat. 1,882,279 (Oct. 11, 1932). Enzymes employed in this manner decompose or alter the composition of ordinary soil and render the soil particles more easily removable with the use of conventional washing products.

However, when enzymes are stored for long periods of time in such a detergent environment, especially in hot and humid climates, a large portion of the enzymes are degraded and/or deactivated. Enzymes used in conjunction with most oxygen bleaches are also easily degraded and/or deactivated when stored for long periods. These problems have been recognized by at least one enzyme manufacturer. See Alcalase, an industrial bulletin published by Novo Industri, A/S, Copenhagen, Denmark.

Successful methods of increasing enzyme stability at ordinary storage temperatures and humidities are documented in the copending U.S. patent applications of McCarty, "Enzyme-Containing Detergent Compositions and a Process for Conglutination of Enzymes and Detergent Compositions," Ser. No. 635,293, filed Apr. 12, 1967 (hereinafter cited as McCarty), and Roald and De Oude, "Granular Enzyme-Containing Laundry Compositions," Ser. No. 630,199, filed Apr. 12, 1967 (hereinafter cited as Roald et al.), now U.S. Pat. 3,451,935.

SUMMARY OF THE INVENTION

The primary object of this invention is to provide an enzyme-containing granular detergent composition wherein the enzymes are stable during long storage periods and particularly wherein the enzymes are stable during long storage periods at high temperatures and high humidities.

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The primary object and other objects which will become apparent from reading the specification are obtained with a granular, enzyme-containing detergent composition comprising, by weight of the detergent composition:

- (1) from about 60% to about 98% of detergent granules comprising polymeric builder salts and organic detergents, the ratio of polymeric builder salts to organic detergents in the detergent composition of this invention ranging from about 30:1 to about 1:4;
- (2) from about 0.001% to about 1.0% of enzymes which are active in the pH range of from about 5.0 to about 11.0 and in the temperature range of from about 50° F. to about 170° F.; and
- (3) environmental control components selected from the group consisting of, by weight of the detergent composition:
 - (a) from about 5% to about 30% of sodium perborate trihydrate;
 - (b) from about 4% to about 15% of components which hydrate at below about 50% relative humidity selected from the group consisting of anhydrous trisodium phosphate, anhydrous calcium sulfate, and mixtures thereof;
 - (c) mixtures of from about 5% to about 30% of component (a) and from about 4% to about 15% of components (b); and
 - (d) proteins in an effective amount to stabilize the enzymes in the granular detergent composition, said proteins having a molecular weight of between about 5,000 and 1,000,000 and being soluble or dispersible in water, in combination with components selected from the group consisting of from about 5% to about 30% of component (a) hereinbefore described; from about 4% to about 15% of components (b) hereinbefore described; and mixtures of from about 5% to about 30% of component (a) and from about 4% to about 15% of components (b).

This invention is particularly designed to increase the storage life or stability of enzymes in granular, enzyme-containing, detergent compositions which are stored and/or used in hot, humid climates.

THE DRAWING

The drawing illustrates the effect of relative humidity on enzyme stability when granular, enzyme-containing detergent compositions are stored for nine days at 75° F. and at 90° F. It is apparent from these curves that the enzymes are quite stable at relative humidities of about 50% and below. As the relative humidity is raised, however, degradation and/or deactivation of the enzymes increases. The detergent composition utilized in experiments to obtain this graphic representation was comprised of, in parts by weight, 24 parts sodium alkyl benzene sulfonate derived from tetrapropylene, 24 parts sodium tripolyphosphate, 5.4 parts sodium silicate (SiO₂:Na₂O ratio of 2:1), 24.3 parts sodium sulfate, 2.5 parts sodium toluene sulfonate, 10 parts sodium perborate tetrahydrate, 9.1 parts water, and 0.7 part Alcalase. The initial enzyme activity reading of 105% may represent minor analytical error or may indicate a minor error in the initial preparation of the enzyme-containing granular detergent composition.

DETAILS AND DESCRIPTION OF THE INVENTION

The granular, enzyme-containing detergent composition of this invention is comprised of three major ingredients: the detergent granules, the enzymes and the environmental control components. These ingredients are described hereinafter. All parts, percentages and ratios set

forth in the specification, the examples and the appended claims are by weight unless otherwise indicated.

DETERGENT GRANULES

The bulk of the granular, enzyme-containing detergent composition of this invention, i.e., from about 60% to about 98%, preferably from 70% to 95%, is made up of ordinary detergent granules comprising polymeric builder salts and organic detergents. The polymeric builder salts are selected from the group consisting of polyphosphate, polyphosphonate, polyacetate and polycarboxylate builder salts or mixtures thereof. The polyphosphate builder salts are exemplified by the sodium and potassium salts of triphosphoric acid.

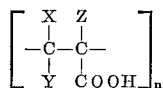
Polyphosphonates are also valuable builders in terms of the present invention including specifically sodium and potassium salts of methylene diphosphonic acid, sodium and potassium salts of ethylene diphosphonic acid, sodium and potassium salts of ethane-1-hydroxy-1,1-diphosphonic acid and sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Other examples include the water soluble [sodium, potassium, ammonium and substituted ammonium (substituted ammonium, as used herein, includes mono-, di-, and triethanol ammonium cations)] salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxymethanediphosphonic acid, carbonyldiphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,3,3-tetraphosphonic acid, propane-1,1,2,3-tetraphosphonic acid, and propane-1,2,2,3-tetraphosphonic acid.

Examples of the above polyphosphonic compounds are disclosed in U.S. Pats. 3,159,581 and 3,213,030 and U.S. Pat. applications, Ser. No. 266,055, filed Mar. 18, 1963, and now U.S. Pat. 3,422,021; Ser. No. 368,419, now abandoned, filed May 18, 1964; Ser. No. 517,073, filed Dec. 28, 1965, and now U.S. Pat. 3,422,137; Ser. No. 507,662, filed Nov. 15, 1965, and now U.S. Pat. 3,400,176; and Ser. No. 489,637, filed Sept. 23, 1965, and now U.S. Pat. 3,400,148.

The polyacetate builder salts suitable for use herein include the sodium, potassium, lithium, ammonium and substituted ammonium salts of the following acids: ethylenediaminetetraacetic acid, N-(2-hydroxyethyl)-ethylenediaminetriacetic acid, N-(2-hydroxyethyl)-nitrilotriacetic acid, diethylenetriaminepentaacetic acid, 1,2-diaminocyclohexanetetraacetic acid and nitrilotriacetic acid. The trisodium salts of the above acids are generally and preferably utilized herein.

The polycarboxylate builder salts suitable for use herein consist of water-soluble salts of polymeric aliphatic polycarboxylic acids selected from the group consisting of:

(a) Water-soluble salts of homopolymers of aliphatic polycarboxylic acids having the following empirical formula:

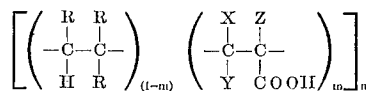


wherein X, Y and Z are each selected from the group consisting of hydrogen, methyl, carboxyl and carboxymethyl, at least one of X, Y and Z being selected from the group consisting of carboxyl and carboxymethyl, provided that X and Y can be carboxymethyl only when Z is selected from carboxyl and carboxymethyl, wherein only one of X, Y and Z can be methyl, and wherein n is a whole integer having a value within a range, the lower limit of which is three and the upper limit of which is determined by the solubility characteristics in an aqueous system;

(b) Water-soluble salts of copolymers of at least two of the monomeric species having the empirical formula described in (a); and

(c) Water-soluble salts of copolymers of a member selected from the group of alkenes and monocarboxylic acids with the aliphatic polycarboxylic compounds de-

scribed in (a), said copolymers having the general formula:



wherein R is selected from the group consisting of hydrogen, methyl, carboxyl, carboxymethyl and carboxyethyl; wherein only one R can be methyl; wherein m is at least 45 mole percent of the copolymer; wherein X, Y and Z are each selected from the group consisting of hydrogen, methyl, carboxyl and carboxymethyl; at least one of X, Y and Z being selected from the group of carboxyl and carboxymethyl provided that X and Y can be carboxymethyl only when Z is selected from the group of carboxyl and carboxymethyl, wherein only one of X, Y and Z can be methyl and wherein n is a whole integer within a range, the lower limit of which is three and the upper limit of which is determined primarily by the solubility characteristics in an aqueous system; said polyelectrolyte builder material having a minimum molecular weight of 350 calculated as the acid form and an equivalent weight of about 50 to about 80, calculated as the acid form, (e.g., polymers of itaconic acid, aconitic acid; maleic acid; mesaconic acid; fumaric acid; methylene malonic acid; and citraconic acid and copolymers with themselves and other compatible monomers such as ethylene). These polycarboxylate builder salts are more specifically described in U.S. Pat. 3,308,067, issued Mar. 7, 1967 to Francis L. Diehl entitled "Polyelectrolyte Builders and Detergent Compositions."

Mixtures of the above-described polymeric builder salts can be utilized to advantage in this invention.

The organic detergents suitable for use herein include soap, anionic synthetic detergents, nonionic synthetic detergents, zwitterionic synthetic detergents and ampholytic synthetic detergents and mixtures thereof. These organic detergents are described in detail in U.S. Pat. 3,351,558 issued Nov. 7, 1967 to Roger Earl Zimmerer entitled "Detergent Composition Containing Organic Phosphonate Corrosion Inhibitors," starting at column 6, line 59 and ending at column 9, line 74.

It is preferred that these detergent granules, when utilized in this invention, be dried to a total moisture content of less than 8%.

The detergent granules utilized in this invention are generally comprised of organic detergents and polymeric builder salts; however, detergent granules comprising only organic detergents or only polymeric builder salts can be utilized herein specialized applications, e.g., detergent granules comprising only polymeric builder salts can be utilized as enzyme carriers in this invention. The weight ratio of organic detergents to polymeric builder salts in the detergent composition of this invention ranges from about 4:1 to 1:30, preferably from 1:1 to 1:15. The granules generally range in size from about 100% through a Tyler Standard 6 mesh screen (3.33 mm.) to about 100% on a Tyler Standard 200 mesh screen (0.074 mm.) Segregation of granules in the detergent composition is minimized when the particle sizes range from about 100% through a Tyler Standard 12 mesh screen (1.40 mm.) to about 100% on a Tyler Standard 100 mesh screen (0.15 mm.) and, therefore, these particle sizes are preferred. The bulk density of the detergent granules, in order to inhibit segregation, generally ranges from about 0.2 gms./cc. to about 0.8 gms./cc.

The detergent granules utilized in this invention can be formed by a variety of well-known methods. For example, the various detergent ingredients can be incorporated into a detergent slurry and spray dried. The detergent granules can also be obtained by agglomerating powders of the various detergent ingredients.

5 ENZYMES

Enzymes suitable for use in this invention which degrade or alter one or more types of soil are large in number and can be grouped into five large classes on the basis of the reactions which they perform in such degradation or alteration. These broad classifications of enzymes are described with particularity in McCarty, at pages 5 through 15 (these pages are specifically incorporated by reference herein). These enzymes, to be useful herein, must be relatively stable in detergent solutions and must be instrumental in removing soil and/or stains from fabrics. Therefore, these enzymes should be active at a pH ranging from about 5 to about 11 and at temperatures ranging from about 50° F. to 170° F. As used herein, enzyme activity refers to the ability of an enzyme to perform the desired function of soil attack and enzyme stability refers to the ability of an enzyme to remain in an active state.

The enzymes suitable for use herein should also be relatively stable when stored in the packaged granular detergent composition of this invention. Degradation and/or deactivation of the enzymes can be inhibited or minimized by incorporating the enzymes with the detergent granules in accordance with the teachings of copending United States patent applications, Roald et al. and McCarty. The enzymes can also be dry-mixed with the detergent components.

Among the many enzyme classes and examples of enzymes discussed in McCarty, the proteases and α -amylases are preferred for use in this invention.

All of the α -amylases show optimum activity in the acid range and are particularly well suited for breaking down starch molecules as they attack the $\alpha_{1,4}$ -glycosidic linkages in starch. The remaining shorter chains are easily removed with aqueous solutions of detergents. The α -amylases may be obtained from animal sources, cereal grains, bacterial or fungal sources. α -Amylase compositions which are commercially available can be utilized herein. Specific examples of these compositions include Wallerstein bacterial α -amylase; Miles α -amylase; Nono α -amylase; Diastatic H-39; Midwest Biochemical α -amylase.

The proteases are generally classified as alkaline proteases, neutral proteases and acid proteases. These classifications indicate the pH range in which optimum enzyme activity is obtained. The alkaline proteases are preferred for use herein. For a more complete discussion of the alkaline, neutral and acid proteases, see McCarty, "Stabilized Aqueous Enzyme Preparation," Ser. No. 683-196, filed Nov. 15, 1967, at page 6.

The proteases catalyze the hydrolysis of the peptide linkage of proteins, polypeptides and related compounds. Free amino and carboxyl groups are thus obtained and the long chain protein structure is reduced to several shorter chains which can be removed from fabrics with ordinary detergent compounds.

Specific examples of proteases suitable for use in this invention are pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, subtilisin, BPN' papain, ficin, bromelain, carboxy peptidase, amino peptidase, aspergillopeptidase A and aspergillopeptidase B and those proteolytic enzymes isolated from streptomyces species. Preferred proteases are subtilisin, BPN', and those proteases isolated from streptomyces species.

Protease composition commercially available can be utilized in this invention. The commercial enzyme compositions containing proteases are generally sold in a powdered form and are comprised of active enzymes in combination with relatively inert ingredients such as sodium or calcium sulfate or sodium chloride. Specific examples of these commercial compositions and the manufacture thereof include: Alcalase; Maxatase; Protease B-4000 and Sandoz AP and AP 2100; CRD-Protease (includes some α -amylase); Pronase-E, Pronase-P;

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Pronase-AS and Pronase-AF; Bioprase (includes some and proteolytic enzyme 7XB; P-11 concentrate, Rhozyme PF, Rhozyme J-25; and Wallerstein 627-P.

CRD Protease, Pronase-P, Pronase-AS, Pronase-AF and Alcalase are more specifically described in McCarty at pages 12-13. (These pages are specifically incorporated by reference herein.)

Large variations in the amount of enzymes in the detergent composition of this invention are contemplated. The detergent composition can contain from about 0.001% to about 1% of enzymes by weight of the detergent composition of this invention. For best results, the detergent composition should contain from about 0.01% to about 0.5% enzymes by weight. When one of the preferred enzyme compositions is utilized in this invention, the granular detergent composition preferably contains from about 0.1% to about 4% of the enzyme composition as it is sold in commercial form, e.g., from about 2% to about 80% active enzymes. The remainder of the enzyme composition is generally comprised of inert ingredients as discussed hereinbefore.

ENVIRONMENTAL CONTROL COMPONENTS

The environmental control components of this invention are beneficial additives to granular, enzyme-containing, detergent compositions because they inhibit or impede degradation and/or deactivation of the enzymes. Degradation as used herein refers to a breakdown or destruction of the protein structure of the enzymes while deactivation refers to alterations of the active sites of enzymes which change or inhibit normal enzyme activity. Degradation and/or deactivation of enzymes in a granular detergent composition is inhibited or impeded by maintaining the relative humidity in the packaged detergent composition as low as possible, preferably below about 50% (see the drawing). This stabilization effect (prevention of degradation and/or deactivation) is further enhanced by complexing the enzymes with a protein which is soluble or dispersible in water to impede autolysis and/or oxidation.

The environmental control components suitable for use herein which inhibit or impede degradation and/or deactivation of enzymes in a granular detergent composition are selected from the group consisting of, by weight of the granular detergent composition:

(a) From about 5% to about 30% of sodium perborate trihydrate;

(b) From about 4% to about 15% of components which hydrate at below about 50% relative humidity selected from the group consisting of anhydrous trisodium phosphate, anhydrous calcium sulfate and mixtures thereof;

(c) Mixtures of from about 5% to about 30% of component (a) and from about 4% to about 15% of components (b); and

(d) Proteins in an effective amount to stabilize the enzymes in the granular detergent composition, said proteins having a molecular weight of between about 5,000 and 1,000,000 and being soluble or dispersible in water, in combination with components selected from the group consisting of from about 5% to about 30% of said component (a) hereinbefore described; from about 4% to about 15% of said components (b) hereinbefore described; and mixtures of from about 5% to about 30% of component (a) and from about 4% to about 15% of components (b).

The drawing illustrates that degradation and/or deactivation of enzymes in a packaged granular detergent composition is strongly influenced by the relative humidity. The influence of relative humidity on enzyme stability is most apparent at relatively high storage temperatures, e.g., 75° F. to 130° F. At lower storage temperatures, the detrimental effects of relative humidity on en-

zymes are not as readily apparent and do not present serious storage problems.

An important function of the environmental control components of this invention is the control of the relative humidity in the packaged granular detergent composition. This is accomplished by utilizing thermodynamically stable components and components which hydrate at relative humidities below about 50%. These components control the relative humidity of the enzyme environment (the packaged granular detergent composition) and promote enzyme stability. When very harsh storage conditions, e.g., 90° F. and 80% relative humidity, are encountered, the relative humidity in the packaged granular detergent composition of this invention may rise considerably, especially where protective packaging is not utilized. Even though the relative humidity of the packaged granular detergent composition of this invention may rise above the optimum of about 50% relative humidity under harsh storage conditions, the relative humidity of the packaged composition of this invention is still considerably below the relative humidity of a similar packaged granular detergent composition which does not contain the environmental control components of this invention. The packaged granular detergent composition of this invention thus provides an environment in which degradation and/or deactivation of enzymes is decreased and enzyme stability is promoted.

To obtain optimum whitening and stain removal without the harsh effects of hypochlorite bleaches, oxygen bleaches are generally added to granular detergent compositions. The most commonly used oxygen bleaches are sodium perborate monohydrate and sodium perborate tetrahydrate. Unfortunately, the addition of these sodium perborate hydrate species to enzyme-containing detergent compositions, especially when these detergent compositions are stored at high temperatures, can cause degradation and/or deactivation of the enzymes. Sodium perborate tetrahydrate is thermodynamically unstable and, when subjected to temperatures of more than about 90° F., rapidly loses water of hydration to the atmosphere. Release of water in a packaged, granular, enzyme-containing detergent composition significantly increases the relative humidity in the package and causes degradation and/or deactivation of the enzymes. Sodium perborate monohydrate, when utilized in enzyme-containing detergent compositions, also causes deactivation and/or degradation of enzymes. It is believed that this hydrate species competes vigorously for available water and forms the tetrahydrate. When subjected to heat, the tetrahydrate breaks down with the before-mentioned consequences. The mechanism of degradation and/or deactivation of the enzymes is not known with certainty although it is believed that the enzymes are degraded through a combination of enzyme autolysis (self-destruction) and oxidation. The enzymes are oxidized in such a manner that the function of the active enzyme sites is detrimentally altered.

According to this invention, this beneficial oxygen bleaching is obtained without the detrimental increase in relative humidity and concomitant enzyme degradation and/or deactivation by utilizing from about 5% to about 30% of thermodynamically stable sodium perborate trihydrate instead of the detrimental sodium perborate hydrate species above described. Sodium perborate trihydrate is not readily convertible to the thermodynamically unstable tetrahydrate form and does not release its water of hydration until temperatures of about 130° F. are attained. This hydrate form is compatible with ordinary detergent ingredients and, additionally does not as readily alter the environment of the enzymes and, thus, cause degradation and/or deactivation of the enzymes utilized in the granular detergent composition of this invention.

Sodium perborate trihydrate is generally manufactured in a finely-divided powder form. To prevent segregation of the sodium perborate trihydrate particles in the

granular, enzyme-containing detergent composition of this invention, sodium perborate trihydrate agglomerates can be formed. The sodium perborate trihydrate particles can be formed into agglomerates of approximately the same size and density as the detergent granules by coating those particles with a normally solid, liquified nonionic detergent (for examples of suitable nonionic detergents, see McCarty at pages 17 through 21; these pages are specifically incorporated by reference herein); glue (for example, dextrin), or an aqueous solution of sodium silicate and agglomerating the particles in a cement mixer, pan agglomerator or similar equipment.

The sodium perborate trihydrate particles, or preferably agglomerates, are generally dry-mixed into the detergent composition of this invention. These particles or agglomerates can be incorporated into the detergent granules but such incorporation is not generally practiced because of the difficult processing problems involved.

When sodium perborate trihydrate is utilized in the granular, enzyme-containing detergent composition of this invention, it is preferred that other oxygen bleaches not be utilized in conjunction therewith.

According to this invention, the relative humidity in the packaged detergent composition can be controlled by the addition of from about 4% to about 15%, preferably from 7% to 15%, of components which hydrate at relative humidities below about 50%. These components are selected from the group consisting of anhydrous trisodium phosphate, anhydrous calcium sulfate and mixtures thereof. The preferred component for use herein is anhydrous trisodium phosphate.

These components are most preferably dry-mixed into the detergent compositions. They preferably are not an integral portion of the granules to which enzymes are attached because these components tend to draw moisture to themselves. If these components were an integral part of the granules to which the enzymes were attached, they might also draw moisture to the enzymes with concomitant degradation and/or deactivation of the enzymes.

Combinations of sodium perborate trihydrate and anhydrous trisodium phosphate, anhydrous calcium sulfate or mixtures thereof can also be used herein. They are utilized in the amounts set forth above, i.e., from about 5% to about 30% of sodium perborate trihydrate and from 2% to 15% of components selected from the group consisting of anhydrous trisodium phosphate, anhydrous calcium phosphate and mixture thereof. The enzyme stabilizing effect is additive.

Proteins having a molecular weight of between about 5,000 and 1,000,000 which are soluble or dispersible in water are utilized herein in an effective amount to stabilize the enzymes in the granular detergent composition in combination with the above described sodium perborate trihydrate and/or anhydrous trisodium phosphate, anhydrous calcium sulfate or mixtures thereof in the amounts set forth above. Examples of proteins which are soluble or dispersible in water and suitable for use herein include casein (average molecular weight 50,000 to 200,000), Wilson Protein WSP-X-1000 (a solubilized collagen having an average molecular weight of 10,000), Knox® gelatin, alpha protein (soy protein), gelation, zein, collagen and albumins such as bovine albumin and egg albumin. Wilson Protein WSP-X-1000 is especially preferred for use herein. These proteins are preferably utilized herein in a weight ratio of proteins to enzymes of from about 1:1 to about 10:1.

The proteins utilized herein are generally obtained in a powdered form and this form is preferred for use herein. It is important that the proteins utilized herein be soluble or dispersible in water. These properties, i.e., solubility and dispersibility, facilitate complexing the enzyme and the protein and inhibit deposition of proteins on fabrics being laundered with concomitant yellowing of the fabrics. Aqueous solutions or dispersions of proteins can also be utilized herein.

While not wishing to be bound by any particular theory, it is believed that the proteins, as described above, are instrumental in preventing autolysis and/or oxidation of the enzymes. It is believed that autolysis and oxidation are prevented by the formation of an enzyme-protein complex. The enzymes, in this complexed form, are protected from oxidation and are separated from each other thereby preventing autolysis. When this enzyme-protein complex is exposed to water or aqueous detergent solutions, however, the complex is severed and the enzymes can then act on soil clinging to the fabrics being laundered. Because this enzyme-protein complex is easily severed on contact with moisture, the relative humidity in the package should be controlled, preferably with the use of the hereinbefore described environmental control components.

The protein is preferably incorporated into the detergent composition of this invention by mixing the enzymes and the protein with water and spraying this mixture onto a portion of the detergent granules. These detergent granules can be specially formulated to contain primarily polymeric builder salts or they can have a composition similar to the rest of the detergent granules. By utilizing this method, contact between the enzymes and the protein is assured and maximum stabilizing of the enzymes is obtained.

The proteins can be mixed with the enzymes by other methods. The proteins and enzymes can simply be dry mixed into the detergent composition or they can be mixed with all of the various ingredients, selected ingredients or a portion thereof of the detergent composition in the presence of water, liquified nonionic detergents (such as those described in McCarty at pages 17 through 21) or the like to form agglomerates.

The proteins are utilized in a granular, enzyme-containing detergent composition in combination with sodium perborate trihydrate and/or anhydrous trisodium phosphate, anhydrous calcium sulfate or mixtures thereof. When proteins are utilized in combination with these components, enzyme stabilization is enhanced.

To maintain optimum environmental conditions and to obtain maximum enzyme stability in the granular enzyme-containing detergent composition of this invention, a moisture resistant package should be utilized. The package is important, especially when the temperature and humidity are high, in preventing large amounts of moisture which cannot be assimilated by the environmental control components described above from entering the detergent package from the atmosphere. Examples of packages which are preferably utilized in commercial applications of this invention are foil wrapped cartons, asphalt laminated cartons, outer wax laminated cartons and polyethylene bags. Even when the package is not moisture resistant, the detergent composition of this invention is stable for a longer period of time than a comparable detergent composition which does not contain the environmental control components hereinbefore described.

EXAMPLES

The following examples merely serve to illustrate the invention in specific detail and when read in conjunction with the foregoing description will aid in determining the scope of the present invention. The examples are merely illustrative and are not meant to restrict the invention.

Example I

Spray-dried detergent granules were prepared comprising the following ingredients:

Ingredient—	Parts by weight
Sodium alkyl benzene sulfonate derived from tetrapropylene	24.0
Sodium tripolyphosphate	18.6
Sodium silicate (SiO ₂ :Na ₂ O ratio of 2:1)	5.4
Sodium sulfate	24.3
Sodium toluene sulfonate	2.5
Water	6.2
Total	81.0

A mixture of water and Alcalase was sprayed onto anhydrous sodium tripolyphosphate in accordance with the method described in Example V of Roald et al. at pages 35 and 36 to obtain an enzyme-carrier composition comprising 0.5 part Alcalase (6% crystalline enzyme), 5.4 parts sodium tripolyphosphate, and 1.1 parts water.

81.0 parts of the detergent granules were mixed with 10 parts of sodium perborate trihydrate and 7.0 parts of the enzyme-carrier composition to form Composition A.

Control detergent compositions were prepared containing, as replacements for sodium perborate trihydrate, sodium perborate tetrahydrate (Composition B) and sodium perborate monohydrate (Composition C). The replacements were made on an equal oxygen basis.

Compositions A, B and C were each separated into two equal portions and these portions were placed in separate sealed glass jars. Portions of Compositions A, B and C were stored at 90° F. and other portions of these compositions were stored at 110° F. The relative humidity outside the glass jars was about 80%. At the beginning of this experiment, the relative humidity inside the glass jars was about 50%. The relative humidity outside of the glass jars did not influence this test because the jars were sealed. The results are summarized in the following table:

TABLE 1

Composition:	Hydrate of sodium perborate	Storage temperature, ° F.	Percent remaining activity ¹ after ninety days
A.....	Trihydrate.....	90	79.0
B.....	Tetrahydrate.....	90	70.5
C.....	Monohydrate.....	90	62.0
A.....	Trihydrate.....	110	67.5
B.....	Tetrahydrate.....	110	60.0
C.....	Monohydrate.....	110	58.0

¹ Percent remaining activity of the enzymes was determined by the Azocoll method. The Azocoll method is based on the release of a water-soluble dye from a water-insoluble protein dye substrate (Azocoll) by a proteolytic enzyme. The amount of dye released under carefully controlled conditions is measured spectrophotometrically. Enzymatic activity is calculated from the amount of dye released.

It is evident from the above table that the enzyme activity remaining after ninety days is substantially greater when sodium perborate trihydrate is utilized in the above composition than when sodium perborate monohydrate or sodium perborate tetrahydrate is utilized therein. In both storage tests, 90° F. and 110° F., Composition A containing 10% sodium perborate trihydrate retained at least 10% more enzyme activity after ninety days storage than either Composition B or Composition C. It is believed that the sodium perborate monohydrate and tetrahydrate species caused an increase in the relative humidity in the sealed glass jars with concomitant enzyme degradation and/or deactivation.

Composition A of this example is beneficial in removing stains from fabrics and for general cleaning and whitening of fabrics. It can also be utilized in other washing applications.

Example II

Spray-dried detergent granules were prepared comprising the following ingredients:

Ingredient—	Parts by weight
Sodium alkyl benzene sulfonate derived from tetrapropylene	24.0
Sodium tripolyphosphate	18.6
Sodium silicate (SiO ₂ :Na ₂ O ratio of 2:1)	5.4
Sodium sulfate	24.3
Sodium toluene sulfonate	2.5
Water	6.2
Total	81.0

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A mixture of water and Alcalase was sprayed onto anhydrous sodium tripolyphosphate in accordance with the method described in Example I to obtain an enzyme-carrier composition comprising 0.5 part Alcalase (6% crystalline enzyme), 5.4 parts sodium tripolyphosphate, and 1.1 parts water.

81.0 parts of the spray-dried detergent granules were mixed with 10 parts of sodium perborate tetrahydrate, 7.0 parts of the enzyme-carrier composition, and 10 parts of anhydrous trisodium phosphate to form Composition D. Composition E was prepared containing 81.0 parts of the spray-dried detergent granules, 10 parts of sodium perborate tetrahydrate, 7.0 parts of the enzyme-carrier composition and 5 parts of anhydrous trisodium phosphate. A control detergent composition, Composition F, was prepared having the same ingredients as Composition D except that the 10 parts anhydrous trisodium phosphate of Composition D was left out. Portions of Compositions D, E and F were placed in polyethylene bags and stored at 90° F. and 80% relative humidity for 63 days. The relative humidity in the polyethylene bags at the beginning of this experiment was about 50%. The results are tabulated in the following table:

TABLE 2

Composition:	Trisodium phosphate in parts by weight	Percent remaining activity ¹
D-----	10	79
E-----	5	68
F-----	-----	60

¹ Percent remaining activity of the enzymes was determined by the Azocoll method. See Example I, Table 1, footnote 1 for a more complete discussion of the Azocoll method.

Both composition D, containing 10% anhydrous trisodium phosphate, and Composition E, containing 5% anhydrous trisodium phosphate, retained significantly more enzyme activity after storage for 63 days at 90° F. and 83% relative humidity than did Composition F which contained no anhydrous trisodium phosphate. It is believed that the water of hydration of the sodium perborate tetrahydrate or a portion thereof was released in Compositions D, E and F. In Compositions D and E, this released water of hydration or a portion thereof, was bound as water of hydration by the trisodium phosphate thereby preventing enzyme degradation and/or deactivation. It is believed that the water of hydration which was released in Composition F was responsible for the poor showing of that composition in comparison with Compositions D and E.

Some enzyme degradation and/or deactivation was probably also caused by slight amounts of moisture from the high humidity storage area diffusing through the polyethylene bags. This moisture, or a portion thereof, was bound as water of hydration by the trisodium phosphate in Compositions D and E. In Composition F, this moisture raised the relative humidity with the above-described results.

As environmental conditions become less conducive to enzyme stability, additional portions of the environmental control components described herein become useful. As illustrated in Table 2, enzymes in a granular detergent composition containing 10 parts by weight of anhydrous trisodium phosphate are more stable than enzymes in the granular detergent composition containing 5 parts by weight of anhydrous trisodium phosphate.

Example III

Spray-dried detergent granules are prepared comprising the following ingredients:

Ingredient—	Parts by weight
Sodium alkyl benzene sulfonate derived from tetrapropylene -----	24.0
Sodium tripolyphosphate -----	18.6
Sodium silicate (SiO ₂ :Na ₂ O ratio of 2:1) ----	5.4
Sodium sulfate -----	24.3

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Ingredient—	Parts by weight
Sodium toluene sulfonate -----	2.5
Water -----	6.2
Total -----	81.0

A mixture of water, Alcalase and Wilson Protein WSP-X-1000 protein (partially hydrolyzed and solubilized protein having an average molecular weight of about 10,000) is sprayed onto anhydrous sodium tripolyphosphate in accordance with the method described in Example I to obtain an enzyme-carrier composition comprising 0.5 part Alcalase (6% crystalline enzyme), 0.125 part WSP-X-1000 protein and 5.275 parts sodium tripolyphosphate and 1.1 parts water.

81 parts of the spray-dried detergent granules are mixed with 7 parts of the enzyme-carrier composition and 10 parts sodium perborate trihydrate to form Composition G; 0.125 part casein are utilized in place of the Wilson Protein WSP-X-1000 in Composition G to form Composition H. The detergent compositions are packed separately in polyethylene bags and are stored for 55 days at 90° F. and 80% relative humidity. The combination of protein and sodium perborate trihydrate has a definite stabilizing effect on the enzymes.

Example IV

Spray-dried detergent granules are prepared comprising the following ingredients:

Ingredient—	Parts by weight
Sodium dodecyl benzene sulfonate -----	10
Sodium tallow alkyl sulfate -----	10
Sodium tripolyphosphate -----	50
Sodium silicate (SiO ₂ :Na ₂ O ratio of 2:1) ----	6
Sodium sulfate -----	16
Water -----	8
Total -----	100

Alcalase, Wilson Protein WSP-X-1000 and special enzyme-carrier granules are conglutinated with tallow alcohol ethoxylated with 30 moles of ethylene oxide per mole of tallow alcohol (TAE₃₀) in accordance with the method described in McCarty in Example I at pages 40 to 42 to obtain an enzyme-carrier composition comprising 1.0 part Alcalase (6% crystalline enzyme), 0.2 part Wilson Protein WSP-X-1000, 1.0 part tallow alcohol ethoxylated with 30 moles of ethylene oxide per mole of tallow alcohol, 7 parts sodium tripolyphosphate, 1.0 part sodium dodecyl benzene sulfonate and 1.0 part sodium tallow alkyl sulfate.

100 parts of the spray-dried detergent granules are mixed with 11.2 parts of the enzyme-carrier composition and 10 parts anhydrous trisodium phosphate. The combination of trisodium phosphate and solubilized protein (WSP-X-1000) has a definite stabilizing effect on enzymes in this granular detergent composition.

Example V

Results substantially similar to those in the previous examples are obtained when the following enzymes or commercial enzyme compositions are substituted for Alcalase on an equal weight of enzyme basis: Wallerstein bacterial α -amylase, lot number 4546A; Miles α -amylase; pepsin; trypsin; chymotrypsin; collagenase; keratinase; elastase; subtilisin; BPN'; papain; ficin; bromelin; carboxy peptidase; amino peptidase; aspergillopeptidase A; aspergillopeptidase B; proteolytic enzymes derived from Streptomyces species; Maxatase; Protease B-4000; Sandoz AP 2100; CRD-Protease; Pronase-E; Pronase-P; Pronase-AF; Biopraser; Rapidase 400; Rhozyme PF, proteolytic enzyme 7XB and Wallerstein 627-P.

Results substantially similar to those in the previous examples are obtained in that the enzymes are stabilized when 10 parts anhydrous trisodium phosphate are used

in combination with Composition A of Example I, when 10 parts of sodium perborate trihydrate are used in combination with Composition D of Example II, and when 10 parts of anhydrous trisodium phosphate are used in combination with Composition G of Example III.

Results substantially similar to those in the previous examples are obtained in that the enzymes are stabilized when anhydrous calcium sulfate is substituted for anhydrous trisodium phosphate.

Results substantially similar to those in the previous examples are obtained in that the enzymes are stabilized when the following proteins are substituted on an equal weight basis for WSP-X-1000 and casein: Knox® gelatin, alpha protein, zein collagen, bovine albumin and egg albumin.

Results substantially similar to those obtained in the previous examples are obtained when the following polymeric builder salts are substituted either wholly or in part for sodium tripolyphosphate in that the enzymes are stabilized: sodium, potassium, ammonium, monoethanol ammonium, diethanol ammonium and triethanol ammonium salts of the following acids: ethylene diaminetetraacetic acid; N-(2-hydroxyethyl)-ethylenediaminetriacetic acid; N-(2-hydroxyethyl)-nitrolodiacetic acid; diethylenetriaminepentaacetic acid; nitrilotriacetic acid; ethylene diphosphonic acid; ethane - 1 - hydroxy - 1,1-diphosphonic acid; ethane - 1 - hydroxy - 1,1 - diphosphonic acid; ethane - 1,1,2-triphosphonic acid; ethane-2-carboxy - 1,1 - diphosphonic acid, hydroxymethane-diphosphonic acid, carbonyldiphosphonic acid; ethane - 1-hydroxy - 1,1,2 - triphosphonic acid; ethane-2-hydroxy-1,1,2-triphosphonic acid, propane - 1,1,3,3-tetraphosphonic acid; propane - 1,1,2,3 - tetraphosphonic acid; and propane - 1,2,2,3-tetraphosphonic acid and potassium tripolyphosphate; and salts of polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid and citraconic acid and copolymers with themselves and/or ethylene and/or acrylic acid in, e.g., 1:1 molar ratios and having molecular weights of 75,000; 100,000; and 125,000 (the copolymers with ethylene and/or acrylic acid having equivalent weights, based on the acid form of 65, 70 and 75); in the form of their sodium, potassium, triethanolammonium, diethanolammonium and monoethanolammonium salts.

Results substantially similar to those obtained in the previous examples are obtained when the following organic detergents are substituted, either wholly or in part, for sodium alkyl benzene sulfonate derived from tetrapropylene and sodium tallow alkyl sulfate in that the enzymes are stabilized: sodium linear dodecyl benzene sulfonate, the condensation product of 1 mole of dodecyl phenol with 15 moles of ethylene oxide, dimethyldodecylamine oxide, dimethyldodecylphosphine oxide, 3 - (N,N-dimethyl - N - hexadecylammonio) - 2 - hydroxypropane-1 - sulfonate and sodium - 3 - dodecylaminopropane sulfonate.

Results substantially similar to those obtained in the previous examples are obtained when the following protective packages are substituted for glass jars and polyethylene bags in that the enzymes are stabilized: foil wrapped cartons, asphalt laminated cartons and outer wax laminated cartons.

What is claimed is:

1. A granular, enzyme-containing detergent composition consisting essentially of, by weight of the detergent composition:

(1) from about 60% to about 98% of detergent granules comprising polymeric builder salts and organic detergents, the ratio of polymeric builder salts to organic detergents in the detergent composition of this invention ranging from about 30:1 to about 1:4;

said organic detergents being selected from the group consisting of soaps, anionic synthetic detergents, nonionic synthetic detergents, zwitterionic synthetic detergents; ampholytic synthetic detergents, and mixtures thereof;

(2) from about 0.001% to about 1.0% of proteases which are active in the pH range of from about 5.0 to about 11.0 and in the temperature range of from about 50° F. to about 170° F.; and

(3) a mixture of environmental control components consisting essentially of proteins in an effective amount to stabilize the enzymes in the granular detergent, said proteins having a molecular weight of between about 5,000 and 1,000,000 and being soluble or dispersible in water; and components selected from the group consisting of from about 5% to about 30% of sodium perborate trihydrate; from about 4% to about 15% of compounds which hydrate at below about 50% relative humidity and selected from anhydrous trisodium phosphate, anhydrous calcium sulfate and mixtures thereof; and mixtures of from about 5% to about 30% of sodium perborate trihydrate and from about 4% to about 15% of said compounds which hydrate below about 50% relative humidity.

2. The granular, enzyme-containing detergent composition of claim 1 wherein:

(1) the detergent granules are present in an amount of from 70% to 95%; and

(2) the enzymes are present in an amount of from about 0.01% to about 0.5%.

3. The granular, enzyme-containing detergent composition of claim 1 wherein the polymeric builder salts are selected from the group consisting of polyphosphate, polyphosphonate, polyacetate and polycarboxylate builder salts and mixtures thereof.

4. The granular, enzyme-containing detergent composition of claim 1 wherein the moisture content of the detergent granules is not more than 8% by weight of the detergent granules.

5. The granular, enzyme-containing detergent composition of claim 1 wherein the enzymes are proteases and are selected from the group consisting of subtilisin, BPN', and those proteases isolated from *Streptomyces* species.

6. The granular, enzyme-containing detergent composition of claim 1 wherein the components which hydrate at relative humidities of less than 50% comprise from about 7% to about 15% of the detergent composition.

7. The granular, enzyme-containing detergent composition of claim 6 wherein the component which hydrates at relative humidities of less than 50% is anhydrous trisodium phosphate.

8. The granular, enzyme-containing detergent composition of claim 1 wherein the protein is utilized in a weight ratio of protein to enzymes of from about 1:1 to about 10:1.

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LEON D. ROSDOL, Primary Examiner

W. E. SCHULZ, Assistant Examiner

U.S. Cl. X.R.

195—63; 252—89; 424—94

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,558,498 Dated January 26, 1971

Inventor(s) Jean-Pierre D. B. Eymery and Harold H. Beyer

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

Column 4, line 53, after the word "herein" -- in --
was omitted.

Column 5, line 49, the word "if" should read -- of --.

Column 6, lines 1 and 2, after the word "some" the
following was omitted -- α -amylase; Rapidase 400; HT proteoly
enzyme 200 --.

Signed and sealed this 19th day of October 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents