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3,560,392

DETERGENT COMPOSITIONS CONTAINING ENZYME-STABILIZING COLLAGEN-DE- RIVED PROTEINS

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17 Claims

ABSTRACT OF THE DISCLOSURE

Granular detergent compositions containing a mixture of organic detergent and an alkaline builder salt in a weight ratio of builder salt to organic detergent of about 30:1 to about 1:4; a proteolytic enzyme characterized by enzymatic activity in the pH range of from about 12 at a temperature of about 50° F. to about 200° F.; and a stabilizing amount of a proteinaceous partially hydrolyzed and partially solubilized collagen, said partially hydrolyzed and partially solubilized collagen having an average molecular weight in the range of about 5,000 to about 250,000.

This application is a continuation-in-part of Eymery and Beyer patent application Ser. No. 686,403, "Granular Detergent Composition Containing Enzymes and Environmental Control Components," filed Nov. 29, 1967.

FIELD OF THE INVENTION

This invention relates to enzyme-containing detergent compositions especially adapted to the removal of soils and stains from laundered textile materials. More particularly it relates to proteolytic enzyme-containing detergent compositions having improved enzyme stability under the adverse environmental conditions.

HISTORY OF THE INVENTION

The use of enzymes in admixture with detergent compositions is known. See U.S. Pat. 1,882,279, issued Oct. 11, 1932 to Frelinghusen, for example. Similarly, British Pat. 814,772, issued June 10, 1959, to Rohm & Haas GmbH; East German Pat. 14,296, published Jan. 6, 1958 to Leiboldt; and Jaag, Seifen, Ole, Fette, Wachse 88, No. 24, pp. 789-793 (November 1962) disclose enzymatic detergent containing enzymes. While the precise theory or mechanism as to the manner in which these enzymatic components provide superior cleaning and stain-removing properties is not completely understood, it is believed that the enzymatic components function as catalytic materials in the degradation of proteinaceous soils and stains. It has been found, however, that the storage of enzyme-containing detergent compositions for long periods of time, especially in hot and humid climates, tends to result in the degradation and/or deactivation of the enzymatic component. The use of perborate bleaching compounds has also tended to result in the loss of enzymatic activity. The result of this degradation and/or deactivation has been substantial loss in soil- and stain-removing efficacy.

Numerous attempts have been made in the art to provide suitable means of improving enzyme stability in enzyme-containing detergent compositions. Suitable methods are described in the copending 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;

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Roald and de Oude, "Granular Enzyme-Containing Laundry Compositions," Ser. No. 630,199, filed Apr. 12, 1967; Davis and Wick, "Enzyme-Containing Granular Detergent Composition," Ser. No. 691,205, filed Dec. 18, 1967; and Eymery and Beyer, "Granular Detergent Composition Containing Enzymes and Environmental Control Components," Ser. No. 686,403, filed Nov. 29, 1967. The provision of proteolytic enzyme-containing detergent compositions having improved stability over extended periods of high temperature and high humidity has been hampered at least in part by the fact that the precise manner in which the varied components of detergent compositions and enzymes interreact to result in degradation and/or deactivation of the enzyme is not completely understood. The present invention provides excellent soil- and stain-removing detergent compositions having improved proteolytic enzyme stability over long storage periods at high temperature and high humidity.

OBJECTS

It is an object of the present invention to provide proteolytic enzyme-containing detergent compositions exhibiting superior cleaning and soil- and stain-removing properties in the laundering of textile materials.

It is another object of this invention to provide proteolytic enzyme-containing granular detergent compositions having improved proteolytic enzyme stability over extended periods of storage at high temperature and high humidity.

A further object of the present invention is to provide proteolytic enzyme-containing granular detergent composition having a perborate bleaching compound and being characterized by improved proteolytic enzyme stability.

Other objects of the invention will become apparent by consideration of the invention which is described more fully hereinafter.

SUMMARY OF THE INVENTION

These and other objects of the present invention are attained by the provision of a proteolytic enzyme-containing detergent composition which comprises:

- (1) from about 60% to about 98% of a mixture of an organic detergent and an alkaline builder salt in a ratio of alkaline builder salt to organic detergent of about 30:1 to about 1:4;
- (2) from about 0.001% to about 2.0% of a proteolytic enzyme characterized by enzymatic activity in the pH range of from about 5 to about 12 and in the temperature range of from about 50° F. to about 200° F.; and
- (3) a proteolytic enzyme-stabilizing amount of a partially hydrolyzed and partially solubilized collagen having an average molecular weight of at least about 5,000.

DETAILS AND DESCRIPTION OF THE INVENTION

The granular, proteolytic enzyme-containing detergent compositions of the present invention are comprised by weight of the total composition of about 60% to about 98%, and preferably about 70% to about 95%, of a mixture of organic detergent and water-soluble builder salt. The organic detergents suitable for use in the detergent compositions of the present invention include soap, anionic synthetic detergents, nonionic synthetic detergents, zwitterionic synthetic detergents and amphoteric synthetic detergents, and mixtures thereof.

Examples of suitable detergent compounds which can be employed in accordance with the present invention include the following:

- (a) Water-soluble soaps.—Examples of suitable soaps for use in this invention are the sodium, potassium, ammonium and alkanolammonium (e.g., mono-, di-, and

triethanolammonium) salts of higher fatty acids (C_{10} – C_{22}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

(b) Anionic synthetic nonsoap detergents.—A preferred class can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic, sulfuric acid 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 these anionic synthetic detergent 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 benzene sulfonates, in which the alkyl group can be a straight or branched chain and contains from about 9 to about 15 carbon atoms, preferably about 12–14 carbons; 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 alkyl phenol ethylene oxide ether sulfates, with 1 to 10 units of ethylene oxide per molecule and wherein the alkyl radicals contain from 8 to 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 tuaride in which the fatty acids, for example, are derived from coconut oil; sodium and potassium salts of SO_3 -sulfonated C_{10} – C_{24} α -olefins.

(c) Nonionic synthetic detergents.—One class of nonionic detergents can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. A second class of nonionic detergents comprises higher fatty amides. A third class of nonionic detergents has semipolar characteristics. These three classes can be defined in further detail as follows:

(1) One class of nonionic synthetic detergents is marketed under the trade name of "Pluronic." These detergent 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 insubility, 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 the polyoxyethylene content is about 50% of the total weight of the condensation product.

(2) Alkylphenol-polyethylene oxide condensates are 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 5 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.

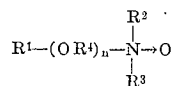
(3) Nonionic synthetic detergents can be derived from

the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine and include 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. Such compounds result from the reaction of ethylene oxide with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000.

(4) Other nonionic detergents include condensation products of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol.

(5) The ammonia, monoethanol and diethanol amides of fatty acids having an acyl moiety of from about 8 to about 18 carbon atoms are useful nonionic detergents. These acyl moieties are normally derived from naturally occurring glycerides, e.g., coconut oil, palm oil, soybean oil and tallow, but can be derived synthetically, e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process.

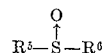
(6) Semipolar nonionic detergents include long chain tertiary amine oxides corresponding to the following general formula



wherein R^1 is an alkyl radical of from about 8 to 18 carbon atoms, R^2 and R^3 are each methyl, ethyl or hydroxyethyl radicals, R^4 is ethylene, and n ranges from 0 to about 10. The arrow in the formula is a conventional representation of a semipolar bond. Specific examples of amine oxide detergents include dimethyldodecylamine oxide and bis(2-hydroxyethyl)dodecylamine oxide.

(7) Other semipolar nonionic detergents include long chain tertiary phosphine oxides corresponding to the following general formula $RR'R''P\rightarrow O$ wherein R is an alkyl, alkenyl, or monohydroxyalkyl radical containing from 10 to 20 carbon atoms 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 semipolar bond. Examples of suitable phosphine oxides are found in U.S. Pat. 3,304,263, which issued Feb. 14, 1967, and include: dimethyldodecylphosphine oxide and dimethyl(2-hydroxydodecyl)phosphine oxide.

(8) Still other simipolar nonionic synthetic detergents include long chain sulfoxides having the formula



wherein R^5 is an alkyl radical containing from about 10 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxyl substituents, at least one moiety of R^5 being any alkyl radical containing 0 ether linkages and containing from about 10 to about 18 carbon atoms, and wherein R^6 is an alkyl radical containing from 1 to 3 carbon atoms and from one to two hydroxyl groups. Specific examples of the sulfoxides are: dodecyl methyl sulfoxide and 3-hydroxy tridecyl methyl sulfoxide.

(d) Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical can be straight chain or branched alkyls and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are

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sodium-3-dodecylaminopropionate and sodium-3-dodecylaminopropane sulfonate.

(e) Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds, in which the aliphatic radical can be straight chain or branched alkyl, and wherein one of the aliphatic substituents contains from about 8 to 24 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato or phosphono. 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-hydroxy propane-1-sulfonate which are preferred for their cool water detergency characteristics. See, for example, Snoddy et al., Canadian Pat. 708,148.

Preferred organic detergents include sodium alkyl benzene sulfonate, sodium alkyl sulfate, and mixtures thereof wherein the alkyl group is of branched or straight chain configuration and contains about 10 to about 18 carbon atoms. Specific examples of preferred organic detergents include sodium decyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium tridecyl benzene sulfonate, sodium tetradecyl benzene sulfonate, sodium hexadecyl benzene sulfonate, sodium octadecyl sulfate and sodium tetradecyl sulfate.

These soap and nonsoap anionic, nonionic, ampholytic and zwitterionic detergent compounds can be used singly or in combination. The above examples are merely illustrations of the numerous suitable detergents. Other organic detergent compounds can also be used.

The alkaline builder salts which can be employed in the detergent compositions of the present invention are employed in an amount to provide a weight ratio of alkaline builder salt to organic detergent of about 30:1 to 1:4, preferably about 15:1 to about 1:1. These builder salts can be selected from a wide variety of known inorganic or organic builder salts. Suitable alkaline, inorganic builder salts include the alkali metal carbonates, phosphates, polyphosphates and silicates. Specific examples of such salts are sodium and potassium tripolyphosphates, carbonates, phosphates and hexametaphosphates.

Suitable organic builder salts include the alkali metal, ammonium, and substituted ammonium polyphosphonates, polyacetates, and polycarboxylates.

The polyphosphonates specifically include sodium and potassium salts of methylene diphosphonic acid, sodium and potassium salts of ethylene diphosphonic acid, sodium and potassium salts of ethane-1,1,2-triphosphonic 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 polyphosphonate compounds are disclosed in U.S. Pat. 3,159,581 and 3,213,030 and U.S. patent applications Ser. No. 266,055, filed Mar. 18, 1963, and now U.S. Pat. 3,422,021; Ser. No. 602,161, filed Dec. 16, 1966; 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.

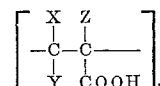
The polyacetate builder salts suitable for use herein include the sodium, potassium, lithium, ammonium and substituted ammonium salts of the following acids: ethylenediaminetetraacetic acid, N-(2-hydroxyethyl)ethylenediaminetriacetic acid, N-(2-hydroxyethyl)nitrilotriacetic acid, diethylenetriaminepentaacetic acid 1,2-diaminocyclo-

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hexanetetraacetic 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:

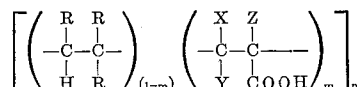
- (a) water-soluble salts of homopolymers of aliphatic polycarboxylic acids having the following empirical formula:



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 alkylenes and monocarboxylic acids with the aliphatic polycarboxylic compounds described 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 builder salts can be utilized to advantage in this invention.

The proteolytic enzymes utilizable in accordance with the present invention are enzymatic materials generally classified in the art as alkaline proteases, neutral proteases and acid proteases. Where used hereinafter in the specification and claims, the designations alkaline proteases, neutral proteases, and acid proteases refer to the pH ranges in which the proteolytic enzymes exhibit their greatest proteolytic activity in enzymatic cleaning.

The proteolytic enzymes suitable herein are those which are characterized by enzymatic activity in the pH range of from about 5 to about 12, at temperatures ranging from about 50° F. to about 200° F. As used herein, proteolytic activity refers to the tendency of a proteolytic enzyme to perform the desired function of catalytic alteration or degradation of proteinaceous soils and stains. Stability, as used herein, refers to the tendency of a proteolytic enzyme to retain its enzymatic activity. The alkaline, neutral and acid proteolytic enzymes employed herein are known materials and are described in detail in Ser. No. 683,196, filed Nov. 15, 1967, at page 6 (McCarty, "Stabilized Aqueous Enzymes Preparation"). This description is hereby incorporated by reference.

While the precise mechanism by which proteolytic enzymes function to provide cleaning and stain removing properties is not completely understood, it is believed that the mechanism involves hydrolysis of the peptide linkage of proteins, polypeptides and related compounds present in soils and stains resulting in the formation of free amino and carboxyl groups and the degradation of long-chain protein structures to several shorter chains which can be removed from fabrics by the detergent action of aqueous solutions of organic detergent compounds.

Specific examples of proteolytic enzymes suitable for use in this invention are pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, the subtilisins, papain, ficin, bromelain, carboxy peptidase, amino peptidase, aspergillopeptidase A and aspergillopeptidase B and those proteolytic enzymes isolated from streptomyces species, e.g., *Streptomyces griseus*. Preferred proteolytic enzymes are subtilisins, isolated from the bacterial organism *Bacillus subtilis*, e.g. Carlsberg and BPN' strains, and those proteases isolated from streptomyces species. The amino acid sequences of Carlsberg subtilisin and BPN' subtilisin are described in Smith et al., "The complete Amino Acid Sequence of Two Types of Subtilisin, BPN' and Carlsberg," J. of Biol. Chem., vol. 241, Dec. 25, 1966 at page 5974. (This article is incorporated by reference herein.) Another especially preferred proteolytic enzyme for use herein is the protease obtained from *Anthrobacter* bacteria obtained from Aktiebolaget Astra, Sodertalje, Sweden described in U.S. Pat. 3,345,269, which issued Oct. 3, 1967.

The above described proteases can be utilized in a pure form in the preparation of enzyme-containing detergent compositions. Generally, however, powdered commercial enzyme compositions containing these enzymes are utilized herein. These commercial compositions contain about 2% to about 80% proteolytic enzyme in combination with inert powdered vehicles or fillers which can comprise sodium or calcium sulfate as the remaining 20% to 98%. These commercially available compositions can in addition contain minor amounts of liquid and carbohydrate materials as well as lipase or α -amylase. Lipase and the like are desirable and can contribute to the cleaning process. Specific examples of these commercial compositions and the manufacturer thereof include: Alcalase; Maxatase; Protease B-400 and Sandoz AP and AP 2100; CRD-Protease; Pronase-E, Pronase-P, Pronase-AS and Pronase AF; Bioprase; Rapidase 400; HT proteolytic enzyme 200 and proteolytic enzyme 7XB; P-11 concentrate, Rhozyme PF, Rhozyme J-25; and Wallerstein 627-P.

Pronase-P, Pronase-AS, Pronase-AF, all obtained from *Streptomyces griseus*, and Alcalase and CRD Protease, both obtained from *Bacillus subtilis*, are more specifically described in McCarty, "Enzyme-Containing Detergent Compositions and a Process for Conglutination of Enzymes and Detergent Compositions," Ser. No. 635,293, filed Apr. 12, 1967 at pages 12-13. (These pages are specifically incorporated by reference herein.)

As described hereinbefore, the amount of proteolytic enzyme employed herein in the enzyme-containing deter-

gent compositions of the present invention is about 0.001 to about 2%, and preferably from about 0.01% to about 0.5%, of the composition on a pure enzyme basis. It will of course be appreciated that the amount of enzymatic composition required in the formulation of detergent compositions have a desired level of proteolytic activity varies with the activity level of the enzyme-containing composition employed.

When a source of proteolytic enzyme and inert carrier is employed wherein the active protease is present in a minor amount, e.g., about 2% and, hence, the activity unit value is in the lower region of the operable range, the level of activity can be compensated for by employing a relatively large amount of the enzymatic composition. Similarly, formulation having higher amounts, e.g., 90% proteolytic enzyme can be employed in relatively smaller amounts. The precise amounts of such materials employed in the formulation of enzyme-containing detergent compositions can be readily determined by methods known in the art so long as the requisite amount of protease is employed as hereinbefore specified.

The proteinaceous materials which unexpectedly have been found to have a stabilizing effect on proteolytic enzyme components of detergent compositions are collagen-derived protein materials characterized by average molecular weights in the range of about 5,000 to about 250,000. Suitable collagen-derived proteins herein are those by partial hydrolysis of collagen. As used herein, partially hydrolyzed and partially solubilized collagen proteins are materials derived from collagen sources by partial hydrolytic, digestive degradation with water, acid, alkali, heat, pressure and the like, sufficient to render the collagen soluble or dispersible in water at about room temperature (25° C.) without destroying the essential protein structure of the collagen.

The partially hydrolyzed and partially solubilized proteins useful herein are obtained by digestive hydrolysis of collagen which is found in a number of naturally occurring substances. Collagen consists of high molecular weight proteinaceous heavily cross-linked molecules and is found, for example, in the white fibrous connective tissues in mammals and fish and is localized in major tissues such as skin, tendon and bone. Examples of collagen-containing sources include pigskins, tanner's stock (calf skins not usable for leather) and ossein (tissue from dried cattle bones remaining after acid treatment which removes the calcium phosphate). These collagen-containing sources are treated in a conventional manner to remove fat, mineral matter and noncollagen protein and are digested as hereinbefore described by hydrolyzing the collagen with successive water extractions at temperature, for example, ranging from about 120° F. to about 212° F. The proteinaceous collagen molecules are digested with successive hydrolytic stages to yield partially degraded collagen molecules which retain the amino acid constituency of collagen but which vary in molecular weights and in gelling properties. As the collagen material is hydrolyzed through successive stages of hydrolysis, degradation of the collagen to proteinaceous molecules of decreasingly lower molecular weight and increasingly higher solubility occurs. Generally, higher molecular weight proteinaceous molecules exhibiting gelling properties in water, and generally termed gelatins, are prepared in the first stages of hydrolysis. Nongelling proteinaceous materials of lower molecular weights and increased solubility which still retain the characteristic amino acid constituency of collagen are obtained as the hydrolytic degradative process is continued through successive stages. The partially hydrolyzed and partially solubilized collagen-derived proteins useful herein are those which are derived by hydrolytically digesting collagen such that the proteinaceous materials which result retain substantially the characteristic amino acid constituency of collagen and have an average molecular weight of at least 5,000. Proteins which are completely hydrolyzed in the

sense that partial hydrolysis is used herein have molecular weights below an average of about 5,000 and are not suitable herein. Partially hydrolyzed and solubilized proteolytic enzyme-stabilizing proteins herein are characterized by average molecular weights in the range of about 5,000 to about 250,000. It will of course be appreciated that the hydrolyzed proteinaceous materials useful herein can contain protein molecules below and/or above the stated ranges and that the specified ranges constitute average molecular weights.

The nature of collagen which by hydrolysis provides useful proteolytic enzyme-stabilizing materials herein is described by Veis (Ed.), *Macromolecular Chemistry of Gelatin* (1964), pp. 1-43. The conversion of collagen to gelatins is described by Kramer, "Gelatin—How It's Made," *Food Engineering* (November 1967) at pages 75-77 and by Veis (Ed.), *supra*, at pages 127-218. The further degradation of gelatin to nongelling collagen-derived proteins is described in Veis (Ed.), *supra*, at pages 223-264.

All of the available gelatins having average molecular weights between about 5,000 and about 250,000 and the partially solubilized and hydrolyzed nongelling collagen-derived proteins having an average molecular weight of between 5,000 and 50,000 are suitable for use in this invention and all significantly stabilize the proteases employed herein. It is especially desirable, however, to utilize collagen-derived proteins (both gelling and nongelling proteins) having a molecular weight within the range of from about 5,000 to about 100,000. Partially solubilized and hydrolyzed nongelling proteins having an average molecular weight of 5,000 to 25,000 are highly preferred for use herein.

The collagen-derived proteins utilized herein are generally obtained in a powdered form and this form is preferred for use herein. It is important that these proteins be soluble or dispersible in water. These properties, i.e., solubility and dispersibility, facilitate intimate contact of the protease and protein, as described hereinafter, and minimize the deposition of these proteins on laundered fabrics and the tendency of such deposition to result in the yellowing of such fabrics.

Specific examples of commercial collagen-derived proteins suitable for use herein are: WSP-X-1000 (average molecular weight of 10,000); Knox® Gelatin (average molecular weight of 50,000 to 70,000); and Swift Technical Protein Colloid #I-V (average molecular weight of about 10,000). Collagen-derived protein is available from many different commercial sources and in many average molecular weights ranging from 5,000 to 250,000. Any of these collagen-derived proteins can be used herein.

The collagen-derived proteins described above are employed herein in a proteolytic enzyme-stabilizing amount. Generally, the protein is utilized herein in a weight ratio of protein to pure protease of from about 100:1 to about 1:10, preferably from about 20:1 to about 1:1.

While not wishing to be bound by any particular theory, it is believed that the proteins, as described above, preserve the enzymatic activity of proteolytic enzymes by inhibiting degradation, denaturation, autolysis and/or oxidation of the enzyme. It is believed that degradation, autolysis and denaturation oxidation are minimized by the presence of both proteolytic enzyme and protein in intimate relationship. The enzyme in intimate contact with protective proteinaceous matter is protected from the harmful effects of temperature, humidity and perborate bleaching compounds and resulting degradation, denaturation, autolysis and/or oxidation.

In addition to the organic detergent, builder salt, proteolytic enzyme and partially hydrolyzed and solubilized collagen-derived protein components of the detergent compositions of this invention, the detergent compositions can also contain any of the usual detergent adjuvants, diluents, and additives. For example, perfumes, antir-
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deposition agents, bacteriostatic agents, dyes, fluorescers, suds builders, suds depressors, and the like, can be utilized herein without detracting from the advantageously properties of the composition.

In a preferred embodiment of this invention, sodium perborate tetrahydrate or sodium perborate monohydrate is included in the detergent composition for its bleaching utility. The use of sodium perborate in enzyme-containing detergent compositions was thought to degrade the enzyme. See Leidholdt, East German Pat. 14,296, published Jan. 6, 1958, for example. However, by this invention, protease stabilization is obtained even in the presence of sodium perborate. From about 0% to about 30%, preferably 5% to 25%, by weight of the detergent composition of sodium perborate, e.g., the monohydrate, tetrahydrate, can be used.

In another preferred embodiment of this invention, an acid component such as dihydrogen disodium pyrophosphate, sodium bisulfate, sodium bicarbonate or mixtures thereof is included to provide an enzyme-stabilizing effect. Preferably, the acidic component is employed in combination with a builder salt, and optionally an organic detergent, as a carrier for the proteolytic enzyme hereinbefore described.

The enzyme-containing detergent compositions of this invention can be prepared by methods known to those skilled in the art. For example, the mixture of organic detergent and builder salt employed herein can be employed in the form of spray-dried or agglomerated granules having a moisture content of less than about 8% or can be employed in the form of a mechanical mixture of granular organic detergent and builder salt. The detergent granules can 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 size of the granules ranges 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.); this latter particle size range is preferred. The bulk density of the detergent granules, in order to reduce segregation, preferably ranges from about 0.2 gm./cc. to about 0.8 gm./cc.

The mixture of detergent and builder salt can be mechanically mixed with the proteolytic enzyme and the partially hydrolyzed and solubilized collagen-derived protein components to provide detergent compositions having the advantageous cleaning and soil- and stain-removing properties hereinbefore described.

It is preferred, however, that the proteolytic enzyme and collagen-derived protein components be present in the detergent compositions of the present invention in an intimately contacted form. For example, the enzyme and collagen-derived protein can be mixed with water into a slurry or solution and sprayed onto one or more of the granular components comprising the detergent compositions of this invention to provide enzyme-containing granules. These enzyme-containing granules can be admixed with detergent granules prepared by conventional methods to provide enzyme-containing detergent compositions useful herein. An amount of water in a ratio of water to combined weight of proteolytic enzyme and collagen-derived protein of about 1:2 to about 4:1 is sufficient for preparing these enzyme-containing granules. The granules which can be sprayed as hereinbefore described are comprised of alkaline builder salt, e.g., sodium tripolyphosphate, or a mixture of organic detergent and alkaline builder salt. The proteolytic enzyme and collagen-derived protein can be prepared into an intimately contacted form by other methods such as by agglomeration of the enzyme and collagen-derived protein with a glutinous material such as a liquified nonionic detergent.

In order to preserve the activity of the proteolytic enzyme employed herein, particularly under hot and humid climatic conditions, it is especially preferred to prepare

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enzyme-carrier granules containing the proteolytic enzyme, an acidic component and collagen-derived protein and to admix these enzyme-containing granules with detergent granules prepared by methods known in the art.

The enzyme-containing detergent compositions of this preferred type can conventionally be prepared by dry-mixing about 80% to about 98% detergent granules with about 2% to about 20%, preferably about 2% to about 12% by weight of the enzyme-carrier granules.

These preferred compositions are comprised by weight of the granular detergent composition of:

- (a) about 80% to about 98% of a mixture of an organic detergent and an alkaline builder salt in a ratio of alkaline builder salt to organic detergent of about 30:1 to about 1:4;
- (b) about 2% to about 20% of enzyme-carrier granules having a pH in saturated aqueous solution ranging from about 5 to about 8 and comprising, by weight of the enzyme-carrier granules:
 - (1) from about 30% to about 75% of builder salt as described hereinbefore;
 - (2) about 5% to about 50% of an acid component selected from the group consisting of dihydrogen disodium pyrophosphate, sodium bisulfate, sodium bicarbonate, and mixtures thereof;
 - (3) 0% to about 20% of synthetic organic detergent as described hereinbefore;
 - (4) from about 0.01% to about 50% of a proteolytic enzyme characterized by enzymatic activity in the pH range of from about 5 to about 12 and in the temperature range of from about 50° F. to about 200° F.; and
 - (5) from about 0.5% to about 20% of a proteolytic enzyme-stabilizing partially hydrolyzed and partially solubilized collagen having an average molecular weight of at least 5,000.

The principal portion of these preferred detergent compositions, i.e., from 80% to about 98%, is comprised of detergent granules having a pH in aqueous solution at a concentration of 0.12% by weight (ordinary washing concentration) of from about 8.5 to about 11. This pH range is known to be most effective in washing applications, especially in ordinary laundry situations. These detergent granules are comprised of alkaline builder salts and organic detergents in a ratio of alkaline builder salts to organic detergents of from about 30:1 to about 1:4, preferably from about 15:1 to about 1:1.

The remaining 2% to 20%, preferably from 2% to 12%, of these preferred granular detergent compositions is comprised of enzyme-carrier granules. These enzyme-carrier granules have a pH in saturated aqueous solution ranging from about 5.0 to about 8.0.

These enzyme-carrier granules are especially formulated to have the same size and density characteristics as the predominant detergent granules to inhibit segregation of the enzymes in the packaged detergent composition. Preferably, they contain sodium tripolyphosphate and disodium dihydrogen pyrophosphate. Additionally, the components of these enzyme-carrier granules are so selected as to prevent lowering the efficacy of the detergent granules and of the detergent composition as a whole.

The acidified proteolytic enzyme-carrier granules which are sprayed with an aqueous mixture of enzyme and collagen-derived protein can be simply a dry-mixture of components, an agglomerated mixture or can be spray-dried as described in copending U.S. patent application, Davis and Wick, Enzyme-Containing, Granular Detergent Composition, Ser. No. 691,205, filed Dec. 18, 1967 which is incorporated herein by reference.

To maintain optimum environmental conditions and to obtain maximum proteolytic enzyme stability in the granular, enzyme-containing detergent compositions of this invention, a moisture-resistant package can advance-

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tageously be employed. Preferred moisture-resistant packages include foil-wrapped cartons, asphalt-laminated cartons, outer wax-laminated cartons and polyethylene bags. Further protection from adverse environmental conditions can be achieved by including in the compositions of this invention optional environmental control agents such as sodium perborate trihydrate, anhydrous trisodium phosphate, anhydrous calcium sulfate or mixtures thereof. Even when stored in packages which are not moisture resistant, the detergent compositions of this invention retain their enzymatic activity over a longer period of time than do enzyme-containing detergent compositions which do not contain the collagen-derived protein hereinbefore described.

EXAMPLES

The following examples serve to illustrate the invention in specific detail. The examples are merely illustrative and are not meant to restrict the invention.

Example I

Spray-dried detergent granules having the following formulation were prepared:

Component—	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
Miscellaneous (perfume, brighteners, sodium carboxymethylcellulose) -----	2.0
Total -----	83.0

Ten parts powdered sodium perborate tetrahydrate were uniformly mixed into the above spray-dried detergent granules. This detergent composition had particle sizes ranging from 3.33 mm. to 0.074 mm. and a density of about 0.5 gm./cc.

A slurry containing 1.00 part water, 0.53 part Alcalase (contains 8% active, alkaline Carlsberg subtilisin—remainder is inert materials such as sodium and calcium sulfate) and 0.35 part WSP-X-1000 protein (a powdered, collagen-derived protein having no gelling properties and an average molecular weight of about 10,000) was prepared. This slurry was sprayed onto 5.10 parts of granular, anhydrous sodium tripolyphosphate and these protease-containing granules were mixed uniformly with the above described mixture of spray-dried detergent granules and powdered sodium perborate.

This detergent composition was packed in polyethylene bags and stored at constant conditions of 90° F. and 80% relative humidity for three months. Proteolytic enzyme activity was determined by Azocoll analysis at intervals and compared with that of an enzyme-containing control detergent composition prepared in the same manner but without added WSP-X-1000 protein. The results shown in Table 1.

TABLE 1

	Control		Composition of Example I	
	Analyzed protease level	Percent protease activity remaining	Analyzed protease level	Percent protease activity remaining
Days:				
0 -----	.72	100	.73	100
24 -----	.63	87.5	.66	90
51 -----	.56	78	.69	94
93 -----	.41	57	.62	85
123 -----	.28	39	.69	95

The Azocoll analysis used herein is based on the release of a water soluble dye from a water insoluble protein substrate (Azocoll) by a proteolytic enzyme. The amount of dye released under carefully controlled con-

ditions is measured spectrophotometrically. Protease activity is calculated from the amount of dye released. Normal analytical deviation is apparent in Table 1.

The results of Table 1 show that the enzyme-containing composition of Example I retained its enzymatic activity with little protease degradation under adverse storage conditions for a period of 123 days and in the presence of a perborate bleach. The control suffered about a 60% reduction of protease activity during this time span.

The advantageous stability properties shown in Table 1 were confirmed by washing tests employing swatches containing two different types of stains. The stains utilized were egg stains and EMPA (blood, milk, ink mixture). EMPA 112 swatches were obtained from the Swiss Testing House in St. Gallen, Switzerland (Eidgenossische Material Prüfungsund, Mersuchsanstant für Industrie, Banevesen und Gewenke, Unterstrasse 11, St. Gallen, Switzerland). Detergent compositions employed in these washing tests were the Control (no protein) and the product of Example I, both after storage for 123 days under the above described conditions. Grading of the washed swatches was done on a scale of from 0 to 100 where 0 equals the washing efficacy of a detergent composition having no protease activity and 100 equals the washing efficacy of a freshly prepared protease-containing detergent composition. The average score of the control product was about 25. The product of Example I had an average grade of about 75.

Example II

Spray-dried granules having the following formulation were prepared:

Component—	Parts by weight
Sodium alkyl benzene sulfonate derived from tetrapropylene -----	24.0
Sodium tripolyphosphate -----	18.6
Sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2:1) ----	5.4
Sodium sulfate -----	24.3
Sodium toluene sulfonate -----	2.5
Water -----	6.2
Miscellaneous (perfume, brighteners, sodium carboxymethylcellulose) -----	0.6
Total -----	81.6

Ten parts powdered sodium perborate tetrahydrate were uniformly mixed into the above spray-dried detergent granules.

5.25 parts of granular, anhydrous sodium tripolyphosphate and 1.40 parts of granular, anhydrous disodium dihydrogen pyrophosphate were dry-mixed and employed as proteolytic enzyme carriers. The pH of these enzyme carriers in saturated aqueous solution was 7.7.

A slurry containing 0.5 part Alcalase (contains 8% Carlsberg subtilisin—the remainder is inert materials such as sodium sulfate and calcium sulfate), 0.17 part WSP-X-1000 (a powdered, collagen-derived protein having no gelling properties and an average molecular weight of about 10,000), and 1.05 parts water was prepared and sprayed onto the dry mixture of sodium tripolyphosphate and disodium dihydrogen pyrophosphate, described above. This mixture containing proteolytic enzyme was uniformly mixed with the mixture of spray-dried detergent granules and powdered sodium perborate.

A control detergent composition was prepared having the same composition as that described above except that no WSP-X-1000 protein and no disodium dihydrogen pyrophosphate was included in the Control.

Portions of the control detergent composition and portions of the product of Example II were separately packaged in polyethylene bags and plain cardboard cartons. The polyethylene bags containing these detergent compositions were stored at 90° F. and 80% relative humidity for 90 days. At the end of this storage period, the product of this invention retained about 100% of initial pro-

tease activity and the control composition (without protein or disodium dihydrogen pyrophosphate) retained only 55% of initial protease activity. The combination of disodium dihydrogen pyrophosphate and collagen-derived protein has excellent enzyme-stabilizing effects on granular proteolytic enzyme-containing detergent compositions. The results of storage in plain cardboard cartons after 20 days storage were as follows: the product of Example II retained 70% of initial proteolytic enzyme activity while the control (without protein or disodium dihydrogen pyrophosphate) retained only 17% of initial proteolytic enzyme activity.

Example III

Spray-dried detergent granules of the following composition were prepared:

Component—	Parts by weight
Sodium alkyl benzene sulfonate derived from tetrapropylene -----	24.0
Sodium tripolyphosphate -----	18.6
Sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2:1) --	5.4
Sodium sulfate -----	24.3
Sodium toluene sulfonate -----	2.5
Water -----	6.2
Miscellaneous (perfume, brighteners, sodium carboxymethylcellulose) -----	2.0
Total -----	83.0

Ten parts powdered sodium perborate tetrahydrate were uniformly mixed into the above spray-dried detergent granules.

A slurry containing 1.00 part water, 0.53 part Alcalase (contains 8% active alkaline, Carlsberg subtilisin—remainder is inert materials such as sodium and calcium sulfate) and 0.17 Knox® Gelatin (a powdered, collagen-derived protein having gelling properties and an average molecular weight of about 50,000 to about 70,000) was prepared. This slurry was sprayed onto 5.28 parts of granular, anhydrous, sodium tripolyphosphate and mixed uniformly with the above described mixture of spray-dried detergent granules and powered sodium perborate.

A control product was prepared having the same composition as that described above except that Knox® Gelatin was not included in the formulation.

Portions of the control product and the detergent composition of Example III were packed in polyethylene bags and stored at constant conditions of 90° F. and 80% relative humidity for 90 days with the following results: The product of this invention retained 75% of initial protease activity while the control product retained only 54% of initial activity.

Example IV

Spray-dried detergent granules having the following composition were prepared:

Component—	Parts by weight
Sodium alkyl benzene sulfonate derived from tetrapropylene -----	24.0
Sodium tripolyphosphate -----	18.6
Sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2:1) ----	5.4
Sodium sulfate -----	34.3
Sodium toluene sulfonate -----	2.5
Water -----	6.2
Miscellaneous (perfume, brighteners, sodium carboxymethylcellulose) -----	2.0
Total -----	93.0

A slurry containing 1.02 parts water, 0.53 part Alcalase (contains 8% active alkaline, Carlsberg subtilisin—remainder is inert materials such as sodium and calcium sulfate), and 0.35 part Swift Technical Protein Colloid #I-V (a granular collagen-derived protein having gelling properties and an average molecular weight of about

10,000) was prepared. This slurry was sprayed onto 5.10 parts of granular, anhydrous sodium tripolyphosphate and mixed homogeneously with the above described detergent composition.

A control product was prepared having the same composition as the above described composition except that Swift Technical Protein was not included in the formulation.

The detergent composition was packaged in plain cardboard cartons and stored for 30 days at constant conditions of 90° F. and 80% relative humidity with the following results: the product of Example III retained 58% of its initial proteolytic enzyme activity while the control (without collagen-derived protein) retained only 43% of its initial proteolytic enzyme activity. The stabilization effects of collagen-derived protein on proteolytic enzyme-containing granular detergent compositions is evident.

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

Results substantially similar to those obtained in the previous examples are obtained in that the proteases are stabilized when the following partially hydrolyzed and partially solubilized collagens are utilized herein, WSP-X-1000, Knox® Gelatin, Swift Technical Protein, and collagen-derived proteins having average molecular weights of 180,000, 150,000, 120,000, 80,000, 40,000, 25,000, 10,000 and 5,000.

Results substantially similar to those obtained in Example II are obtained when sodium bisulfate, sodium bicarbonate and mixtures thereof are substituted on an equal weight basis for dihydrogen disodium pyrophosphate in that protease stabilization is enhanced. Substantially similar results are also obtained when the builder component, e.g., sodium tripolyphosphate, and the acid component, e.g., dihydrogen disodium pyrophosphate, are combined in the form of spray-dried granules.

Results substantially similar to those obtained in the previous examples are obtained when the following 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)nitrilotriacetic acid; diethylenetriaminepentaacetic acid; nitrilotriacetic acid; ethylene 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 weight 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).

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.

What is claimed is:

1. A granular proteolytic enzyme-containing detergent composition comprising by weight of the detergent composition:

- (1) from about 60% to about 98% of a mixture of an organic detergent selected from the group consisting of soap, anionic synthetic detergents, nonionic synthetic detergents, zwitterionic synthetic detergents, ampholytic synthetic detergents, and mixtures thereof and an alkaline builder salt in a ratio of alkaline builder salt to organic detergent ranging from of about 30:1 to about 1:4;
- (2) from about 0.001% to about 2.0% of a proteolytic enzyme having enzymatic activity in the pH range of from about 5 to about 12 and in the temperature range of from about 50° F. to about 200° F.; and
- (3) a proteolytic enzyme-stabilizing amount of a partially hydrolyzed and partially solubilized collagen having an average molecular weight of at least about 5,000, said proteolytic enzyme and said partially hydrolyzed and partially solubilized collagen being present in an intimately contacted form on an enzyme carrier granule consisting essentially of alkaline builder salt or a mixture of alkaline builder salt and organic detergent.

2. The composition of claim 1 wherein the partially hydrolyzed and partially solubilized collagen has an average molecular weight of about 5,000 to about 250,000.

3. The composition of claim 2 wherein the mixture comprises from about 70% to about 95% by weight of the detergent composition and contains less than 8% moisture by weight; the proteolytic enzyme comprises from about 0.01% to about 0.5% by weight of the detergent composition; and the partially hydrolyzed and partially solubilized collagen is employed in a weight ratio of said collagen to said proteolytic enzyme of from about 100:1 to about 1:10 and has an average molecular weight of from about 5,000 to about 100,000.

4. The composition of claim 3 which contains from about 0% to about 30% of sodium perborate.

5. The composition of claim 1 wherein the partially hydrolyzed and partially solubilized collagen has an average molecular weight of from about 5,000 to about 25,000 and is employed in a weight ratio of said collagen to said proteolytic enzyme of from about 20:1 to about 1:1.

6. The composition of claim 1 wherein said collagen is gelatin.

7. The composition of claim 1 wherein the proteolytic enzyme is a subtilisin.

8. A granular proteolytic enzyme-containing composition comprising by weight of the detergent composition:

- (a) about 80% to about 98% of a mixture of an organic detergent and an alkaline builder salt in a ratio of alkaline builder salt to organic detergent of about 30:1 to about 1:4; and
- (b) about 2% to 20% of enzyme-carrier granules having a pH in saturated aqueous solution ranging from about 5 to about 8 and comprising by weight of the enzyme-carrier granules;

(1) about 30% to about 75% of alkaline builder salt;

(2) about 5% to about 50% of an acid component selected from the group consisting of dihydrogen disodium pyrophosphate; sodium bi-

sulfate, sodium bicarbonate, and mixtures thereof;

(3) 0% to about 20% of a synthetic organic detergent;

(4) about 0.01% to about 50% of a proteolytic enzyme having enzymatic activity in the pH range of from about 5 to about 12 and in the temperature range of from about 50° F. to about 200° F.; and

(5) about 0.5% to about 20% of a proteolytic enzyme-stabilizing partially hydrolyzed and partially solubilized collagen having an average molecular weight of at least 5,000, said proteolytic enzyme and said proteolytic enzyme-stabilizing partially hydrolyzed and partially solubilized collagen being present on said enzyme-carrier granules in an intimately contacted form.

9. The composition of claim 8 wherein the mixture of organic detergent and alkaline builder salt is a mixture of an organic detergent selected from the group consisting of sodium alkyl benzene sulfonate, sodium alkyl sulfate, and mixtures thereof wherein the alkyl group is of branched or straight chain configuration and contains about 10 to 18 carbons; and an inorganic builder salt selected from the group consisting of sodium tripolyphosphate, sodium pyrophosphate and mixtures thereof in a weight ratio of inorganic alkaline builder salt to organic detergent of about 15:1 to about 1:1.

10. The composition of claim 9 wherein the alkaline builder salt of the enzyme-carrier granules is sodium tripolyphosphate and the acid component is dihydrogen disodium pyrophosphate.

11. The composition of claim 10 wherein the proteolytic enzyme is an alkaline protease and the proteolytic enzyme-stabilizing partially hydrolyzed and partially solubilized collagen has an average molecular weight of about 5,000 to about 100,000.

12. The composition of claim 11 wherein the enzyme-carrier granules comprise from about 2 to about 12% of the detergent composition and the alkaline protease is a subtilisin.

13. A process for preparing a granular proteolytic enzyme-containing composition according to claim 1 comprising contacting a granular component selected from alkaline builder salts and mixtures of alkaline builder salt

and organic detergent with a proteolytic enzyme having enzymatic activity in the pH range of from about 5 to about 12 and in the temperature range of from about 50° F. to about 200° F. and a proteolytic enzyme-stabilizing amount of a partially hydrolyzed and partially solubilized collagen having an average molecular weight of at least about 5,000, thereby to provide an enzyme-carrier granule having said proteolytic enzyme and said partially solubilized and partially hydrolyzed collagen present on said granular component in an intimately contacted form; said organic detergent being selected from the group consisting of soaps, anionic synthetic detergents, nonionic synthetic detergents, zwitterionic synthetic detergents, ampholytic synthetic detergents and mixtures thereof.

14. The process of claim 13 wherein said granular component is sodium tripolyphosphate.

15. The process of claim 14 wherein said proteolytic enzyme and said proteolytic enzyme-stabilizing partially hydrolyzed and partially solubilized collagen are contacted with sodium tripolyphosphate in the form of an aqueous slurry having a ratio of water to combined weight of said proteolytic enzyme and said proteolytic enzyme-stabilizing partially hydrolyzed and partially solubilized collagen of from about 1:2 to about 4:1.

16. The process of claim 15 wherein said aqueous slurry is contacted with sodium tripolyphosphate by spraying said slurry onto said sodium tripolyphosphate with agitation.

17. The granular proteolytic enzyme-containing detergent composition of claim 7 wherein an α -amylase is present.

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U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,560,392 Dated February 2, 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:

first occurrence
[Column 1, line 22, after the word "about"/-- 5 -- was omitted.
Column 7, line 60, "Protease B-400" should read --
Protease B-4000 --.
Column 8, line 40, "proteinaceously heavily" should read
-- proteinaceous heavily --.

Signed and sealed this 12th day of October 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents

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