

United States Patent Office

3,661,786

Patented May 9, 1972

1

3,661,786

DETERGENT COMPOSITIONS CONTAINING STABILIZED α -AMYLASE

Malcolm Desforges, Newcastle-upon-Tyne, England, assignor to The Procter & Gamble Company, Cincinnati, Ohio

No Drawing. Filed Jan. 27, 1970, Ser. No. 6,290

Int. Cl. C11d 7/18, 7/56

U.S. Cl. 252-99

11 Claims

ABSTRACT OF THE DISCLOSURE

A granular detergent composition is provided containing a mixture of an organic detergent and an alkaline builder, an α -amylase, and an amount of starch sufficient to stabilize the α -amylase.

This invention relates to detergent compositions containing α -amylase, which are particularly useful in cleaning textile materials.

In the compositions of the invention, the α -amylase is protected against degradation and denaturation due to adverse conditions which are often encountered during storage. Exposure to temperatures at or above ambient temperatures and/or high humidity (particularly for prolonged periods) tends to destroy or significantly reduce the activity of α -amylase. The activity of α -amylases is also adversely affected by perborate bleaching agents.

Enzyme-containing granular detergent compositions are not new; however, marketable granular detergent compositions with sustained enzymatic activity are a relatively recent development. The use of enzymes in admixture with detergent compositions has been described in U.S. Pat. 1,882,279, British Pat. 814,722, German Pat. 14,296, and E. Jaag: Seifen, Ole, Fette Wachse 88, 789-793 (November 1962).

One of several recent technical innovations has resulted in improved enzyme-containing granular detergent compositions into which the enzymes are incorporated by a method that greatly increases their stability; see British Pat. 1,151,748. In this process, the enzyme is attached to a water soluble granular carrier which is a partially hydrated hydratable salt. Particular enzymes and mixtures of enzymes comprising certain specified alkaline proteases and α -amylases which have superior cleaning properties in granular detergent compositions are described in U.S. SN 721,081, filed April 12, 1968, now abandoned.

Mixtures of α -amylases and proteases that are active under alkaline, acid and neutral conditions are generally effective in commercial applications against a broad spectrum of soils and stains. The addition of a partially hydrolyzed and partially solubilized collagen to protease-containing detergent compositions (which can also contain α -amylase) has been found to stabilize the proteases; see Belgian Pat. 724,567. However, until now, no equally effective method has been discovered for stabilizing α -amylase in detergent compositions. Without the stabilization of α -amylase, its activity is fairly quickly lost during the ordinary marketing of granular detergent compositions.

It has now been discovered that the effective life of α -amylase can be greatly prolonged by a critical amount of starch in intimate contact with the α -amylase in detergent compositions. The starch is a minor additive in these compositions. It can be used alone or in combination with other minor additives such as collagen.

The α -amylase-containing granular detergent compositions of this invention are compositions consisting essentially of, by weight:

- (1) from 40% to 98% of a mixture of an organic detergent and an alkaline builder salt, in a weight ratio of

2

organic detergent to alkaline builder salt of from 1:30 to 4:1;

- (2) from 0 to 50% of a perborate bleaching compound;
- (3) from 0.0005 to 3% of α -amylase (calculated on the basis of pure α -amylase); and
- (4) an α -amylase-stabilizing amount of starch (in addition to any starch which is an inert carrier for the α -amylase) in a weight ratio of added starch to pure α -amylase of from about 1:1 to 5000:1.

Other ingredients can be added to these compositions, for example, in the manner described below. The term "consisting essentially of" is used herein to include minor amounts of ingredients other than those specified above which do not substantially alter the nature of the granular detergent compositions.

α -Amylases are well known enzymes. They are particularly well suited for use in granular detergent compositions because they break down starch molecules by attacking the 1,4 α -glucosidic acid linkages in starchy soils and stains. The resultant shorter molecular chains in these soils and stains are then more readily removed by water or aqueous solutions of detergents. The α -amylases can be obtained from animal, fungal, cereal grain, and bacterial sources.

α -Amylases from *Bacillus subtilis* are preferred because of their ready availability, high activity, a degree of inherent resistance to detergent inactivation and ready stabilization against inactivation in granular detergent compositions in the presence of starch.

Numerous methods have been described for the determination of α -amylase activity. A modification of the saccharifying activity assay developed by P. Bernfeld: Adv. in Enzymology 12, 385 (1951) can be used in the determination of the activity of the α -amylases used in compositions of this invention. In this method, a sample of α -amylase is permitted to catalyze the hydrolysis of the 1,4 α -glucosidic bonds of starch for 5 minutes at a pH of 6.0 and a temperature of 37° C. The reaction is stopped by the addition of an alkaline solution of 3,5-dinitrosalicylic acid and rochelle salt. The brown color of the reduction product which is developed in the analytical sample is compared spectrophotometrically with that developed by standard solutions of maltose hydrate. One amylase activity unit is assigned for each 0.4 mg. of maltose hydrate produced during hydrolysis. In practice, it is found that the amount of maltose produced in the analytical procedure by a substance containing a given amount of α -amylase, and therefore its measured activity in amylase activity units, can vary considerably as a result of slight variations in the test conditions or in the substances with which the α -amylase is associated. The activity of a particular sample can be measured consistently and reproducibly, and values such as those for the percentage amylase activity remaining after a storage test are reliable. While the numerical values of amylase activity quoted in this specification indicate the order of magnitude and are self-consistent, they should not be taken to be exact in absolute terms.

α -Amylases vary in activity depending upon their purity and pH in solution. Pure α -amylase has a specific activity of about 11,500,000 units per gram, while commercially available preparations varying in content of α -amylase have specific activities of about 50,000 to about 1,500,000 amylase activity units per gram. The enzyme-containing detergent compositions of the present invention which contain from 0.0005% to 3% by weight α -amylase (calculated on the basis of pure α -amylase) generally contain from about 60 to about 400,000 amylase activity units per gram of detergent composition.

Commercial α -amylase compositions which can be utilized in this invention include Wallerstein Bacterial α -

Amylase, Lot No. 454A, Wallerstein Company, Staten Island, N.Y.; α -Amylase, Miles Chemical Company, Elkhart, Ind.; the α -Amylase which is an integral part of CRD Protease (Monsanto DA 10) derived from *Bacillus subtilis*. Monsanto Company, St. Louis, Mo., α -amylase, Midwest Biochemical Company, Milwaukee, Wis.; bacterial α -amylase and fungal α -amylase, Novo Industri A/S Copenhagen, Denmark; Maxatase and Maxamyl (trade-marks), Koninklijke Nederlandsche Gist-En Spiritusfabriek N.V., Delft, The Netherlands; and SP. 250, Rapidase, Seclin, France. Mixtures of these materials can be employed in the exercise of the present invention. As more fully explained in above-mentioned U.S. SN 721,081, mixtures of α -amylase and certain alkaline proteases in weight ratios of about 30:1 to about 3:1 of proteases to α -amylase have particularly superior cleaning and stain removal properties when incorporated in granular detergent compositions.

The α -amylase weight content of commercial α -amylase compositions usually varies from about 0.5% to about 15% although some purer grade compositions have a higher α -amylase content. The amount of α -amylase composition which is used depends on its specific activity. More of an α -amylase composition containing 0.5% α -amylase is required in the detergent compositions of this invention than of an α -amylase composition having a higher specific activity.

The inert carriers in which α -amylase is generally sold include starch, calcium and sodium sulfate, sodium chloride and sodium tripolyphosphate. As stated above, the starch which is added to the detergent compositions of this invention is added in addition to any starch which is present in the inert carrier.

The starches which can be used in the detergent compositions of this invention to stabilize the α -amylase may be ordinary granular starches or modified starches including dextrin, which have been obtained from any natural source. The granular starches include, for example, corn starch, potato starch, wheat starch, tapioca starch, rice starch, waxy maize starch and/or sweet potato starch. The physical properties of these starches, such as their granule size, solubility in water, and color vary widely. However, for purposes of achieving the results of this invention, granular starches from any source can be used without regard to their physical properties. It will be apparent, however, that certain starches are more appropriate for commercial purposes because of, for example, their color and ease of handling.

Modified natural starches which have been oxidized by heating (partial pyrolysis) or hydrolyzed with an acid or enzyme can also be used as α -amylase-stabilizing agents. Lintner water soluble starch, for example, is particularly preferred; it is natural starch in which the starch molecules have been modified (decreased in size) by mild acid hydrolysis. Zulkowsky starch can also be used. The molecules of Zulkowsky starch have been modified by heating the starch with glycerol at 190° C. Highly degraded starches such as dextrin (which is prepared by high temperature oxidation) are also suitable for use in this invention. Dextrin is the most soluble of the modified starches and has no granular structure.

The amount of starch to be employed in the granular detergent compositions of this invention can be most easily determined by the activity of the α -amylase. It must, however, fall within the weight ratios of starch to pure α -amylase which have been specified. The best results are achieved when about 0.1 gram to about 6 grams by weight of starch are used per 150,000 amylase activity units, that is, from 8 to 460 gms. starch per gram of pure α -amylase. If the weight percent of α -amylase composition is increased but the activity remains the same, the amount of starch need not be increased. If, however, the amount of α -amylase composition is reduced but the amylase activity is increased, more starch can be required. There is, of course, an amount of starch which should not be exceeded

in granular detergent compositions. Too much starch will unbalance or overload a detergent composition to such an extent that it is impractical either to compose or to use. Most generally, the starch should constitute no more than 10%, and preferably no more than 6%, by weight, of the granular detergent composition.

The organic detergents suitable for use in the detergent compositions of the present invention include soap, anionic synthetic detergents, nonionic synthetic detergents, swifterionic synthetic detergents and ampholytic 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.—Suitable soaps include the sodium, potassium, ammonium and alkanolammonium (e.g., mono-, di-, and triethanolammonium) salts by higher fatty acids (C_{10} – C_{22}). 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, are particularly useful.

(b) Anionic synthetic non-soap detergents.—A preferred class is 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 detergents 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 amides of a methyl taurine 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 includes 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 semi-polar characteristics. These three classes can be defined in further detail as follows:

(1) "Pluronic" (registered trademark) 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 exhibits water insolubility, has a molecular weight of from about 1500 to 1800. 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.

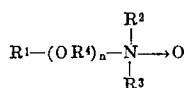
(2) Alkylphenol-polyethylene oxide condensates are condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 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; the base has a molecular weight of about 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.

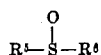
(6) Semi-polar nonionic detergents include long chain tertiary amine oxides corresponding to the following general formula:



wherein R^1 is an alkyl radical of from about 8 to about 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 semi-polar bond. Specific examples of amine oxide detergents include dimethyldodecylamine oxide and bis-(2-hydroxyethyl)dodecylamine oxide.

(7) Other semi-polar nonionic detergents include long chain tertiary phosphine oxides corresponding to the following general formula $\text{RR}'\text{R}''\text{PO}$ 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 semi-polar bond. Examples of suitable phosphine oxides are found in British Pat. 309,841 and include: dimethyldodecylphosphine oxide and dimethyl-(2-hydroxydodecyl)-phosphine oxide.

(8) Still other semi-polar 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 an 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 these 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 about 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 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 British Pat. 987,795.

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 non-soap anionic, nonionic, ampholytic and zwitterionic detergent compounds can be used singularly 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 inorganic or organic in nature and can be selected from a wide variety of known builder salts. The weight ratio of organic detergent to alkaline builder salt is from 1:30 to 4:1 and preferably from 1:9 to 1:1. Suitable alkaline, inorganic builder salts include the alkali metal carbonates, phosphates, polyphosphates and silicates. Specific examples of these salts are sodium or potassium tripolyphosphates, carbonates, phosphates and hexametaphosphates. Suitable alkaline organic builder salts include the alkali metal, ammonium and substituted ammonium polyphosphonates, polyacetates, and polycarboxylates.

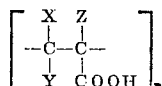
The polyphosphonates specifically include the sodium and potassium salts of ethylene diphosphonic acid, sodium and potassium salts of ethane-1-hydroxy-1,1-diphosphonic acid and sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Other examples include the water-soluble [sodium, potassium, 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, 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. Examples of these polyphosphonic compounds are disclosed in British Pats. 1,026,366; 1,035,913; 1,129,687; 1,136,619; and 1,140,980.

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 preferred.

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

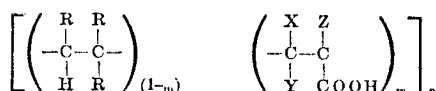
(a) Water-soluble salts of homopolymers of aliphatic polycarboxylic acids having the following empirical formula:



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 described in British Pat. 1,054,755.

Mixtures of the above-described alkaline builders can be used to advantage in this invention.

Perborate bleaching compounds, especially sodium perborate tetrahydrate and/or sodium perborate monohydrate, can be included in amounts up to 50%, preferably from 5 to 40%, of the detergent compositions of this invention. It has been stated that sodium perborate compositions degrade enzymes; see German Pat. 14,296. However, α -amylase can be stabilized in the detergent compositions of this invention even in the presence of a perborate bleaching agent.

In addition to the mixture of organic detergent and alkaline builder salt and the α -amylase and the starch, the compositions of this invention can also contain other

adjuvants, diluents and additives such as perfumes, anti-tarnishing agents, inert salts such as sodium sulfate, anti-redeposition agents, bacteriostatic agents, dyes, fluorocessors, suds builders, suds depressors and the like. The α -amylase-containing granular detergent compositions can be prepared by well known methods; for example, α -amylase and starch or enzymatic mixtures containing α -amylase and starch can be mechanically mixed into formulated detergent compositions. The preferred method, however, is to prepare enzyme carrier granules containing starch and α -amylase (generally in admixture with other enzymes such as proteases) and to admix these granules with other detergent ingredients such as detergent granules and, optionally, a perborate bleaching agent. Compositions of this type can be conveniently prepared by dry mixing about 80% to about 98% detergent granules, comprising alkaline builder salts and organic detergents in the proportions hereinbefore stated, with about 2% to about 20%, preferably about 2% to about 12%, by weight, of the enzyme carrier granules. A perborate bleaching compound can be substituted for a portion of the detergent granules; thus, up to 50%, and preferably 5% to 40%, by weight, of the overall composition can be sodium perborate.

The detergent granules are formed by well known spray drying processes or by agglomeration such that the particle size of the granules is generally from 0.1 mm. to 2.0 mm. and their density generally ranges from 0.2 gm./cc. to 0.8 gm./cc. The detergent granules have a pH in aqueous solution in a concentration of about 0.12%, by weight, ranging from about 8.5 to about 11.

The enzyme carrier granules should have substantially the same size and density as the detergent granules, to inhibit segregation of the detergent granules and the enzyme carrier granules. The enzyme carrier granules can also be prepared by spray drying or coagglomeration methods. Preferred methods are those in which the enzyme and starch are intimately mixed together in solution or in a slurry. In the spray drying method about 20% to about 90% sodium tripolyphosphate or mixtures of sodium tripolyphosphate and sodium pyrophosphate are mixed with about 10% to about 80% of an anionic synthetic detergent such as sodium alkyl benzene sulfonate, sodium alkyl sulfate or mixtures thereof, and water to form a slurry. This slurry is then spray dried to a moisture content of about 1% to about 7%, preferably from about 1.5% to about 4%. An aqueous slurry of α -amylase and starch with or without other enzymes, stabilizing agents such as collagen, and dyes is then prepared and is sprayed onto the carrier granules. The water in the enzyme-containing slurry is bound as water of hydration to the carrier granules. No more than about 7% water should be present in the enzyme carrier granules after the enzyme-containing slurry is sprayed onto the granules and the granules are dried. A more detailed description of this basic process for preparing enzyme carrier granules can be found in British Pat. No. 1,151,748.

An alternative method of preparing the enzyme carrier granules which has been found to be very satisfactory is to prepare a slurry in a liquid, preferably water, of the amylase enzyme material and the starch, optionally to-

gether with other enzymes, such as proteases, stabilizers therefor such as collagen, coloring matter, substances for preventing subsequent dustiness of the carrier granules, etc. This slurry is sprayed on to a bed of particles comprising a hydrate forming salt, such as sodium tripolyphosphate or mixtures of sodium tripolyphosphate and sodium pyrophosphates, in a mixing device, such as a pan granulator. Substantially anhydrous sodium tripolyphosphate is the preferred salt. The carrier granules so formed are given time so that the moisture in the slurry can be absorbed by formation of hydrates, and may then be blended with the remainder of a granular detergent composition. Preferably the moisture content of the carrier granules is kept low, usually not over about 10%, but in some cases it can approach that required completely to hydrate the salts.

Generally speaking, a preferred method of preparing the enzyme carrier granules comprises spraying a slurry of the α -amylase and the starch on to incompletely hydrated sodium tripolyphosphate; the resultant granules may then be mixed with the other ingredients of the granular detergent composition.

The enzyme carrier granules generally have a pH in saturated aqueous solution of about 5.0 to about 10.5. When only α -amylases are present, the pH should be in the lower part of this range. This can be achieved by spraying the enzyme-containing slurry onto an acid carrier granule; for example, acid pyrophosphate. When a mixture of α -amylase and proteases is used, it is generally desirable to have a higher pH within the given range because lower pH's are detrimental to the activity of alkaline proteases.

A dye can be used in the enzyme-containing slurry to give the enzyme carrier granules a distinctive color. When they are mixed with the detergent granules, the mixture has a speckled appearance.

In a coagglomeration procedure which can also be used to form part or all of the compositions of this invention, the various detergent ingredients (for example, sodium tripolyphosphate, and anionic synthetic detergent) and the α -amylase and starch are all sprayed with water and formed into agglomerates in a cement mixer, pan agglomerator or the like.

The compositions of this invention can be packed in moisture-resistant packages such as foil-wrapped cartons, asphalt-laminated cartons, wax-laminated cartons and polyethylene bags.

The invention provides a method of cleaning fabrics which comprises washing the fabrics with an aqueous solution of a granular detergent composition according to the invention.

The following examples serve to illustrate the invention.

EXAMPLE I

(a) Spray dried detergent granules having the following composition were prepared in the conventional manner:

Ingredients:

		Parts by weight
A mixture of 65% sodium tallow alkyl sulfate and 35% sodium linear alkyl benzene sulfonate in which the approximate alkyl chain length distribution is 40% C ₁₀ +C ₁₁ ; 20% C ₁₃ ; 10% C ₁₄ ; and the balance is C ₁₂ -----		14.3
Sodium tripolyphosphate -----		44.8
Sodium silicate having an SiO ₂ :Na ₂ O ratio of 1.6:1 -----		6.7
Sodium 80/20 tallow/palm kernel oil fatty acid soap -----		3.8
Sodium sulfate -----		12.3
Sodium toluene sulfonate -----		1.4
C ₁₂ monoethanolamide -----		1.9
Water -----		10.0
Miscellaneous including fluorescers, perfumes, sodium carboxymethylcellulose and ethylenediaminetetraacetic acid, balance.		

100.0

(b) Twenty-five parts by weight of powdered sodium perborate tetrahydrate were uniformly mixed into the above spray dried detergent granules.

(c) A slurry was prepared containing 6.66 parts by weight water, 0.01 part of blue dye (Monastral Blue), 4.00 parts Alcalase enzyme which contained 20% alkaline subtilisin protease enzyme and the balance inert sodium and calcium sulfate, 1.17 parts Monsanto DA-10 which contained about 2.5% α -amylase and an unknown percentage of neutral and alkaline proteases in an inert starch vehicle, and 2.00 parts water soluble Lintner starch. This slurry was sprayed onto 86.16 parts of granular, anhydrous sodium tripolyphosphate; these granules were then uniformly admixed with the spray-dried detergent granules containing the powdered sodium perborate. The resulting composition contained about 5.6 parts by weight of the enzyme-containing granules.

These detergent compositions were packed in conventional moisture barrier cardboard cartons and stored at constant conditions of 90° F. and 80% relative humidity for six weeks. The α -amylase activity was determined at weekly intervals for the first four weeks and at the end of six weeks. The α -amylase activity was compared with that of a control detergent containing no Lintner starch and with those of three other detergent compositions which were similar in all respects to the control detergent and the detergent containing 2% Lintner starch except that the enzyme carrier granules contained 4%, 6% and 8%, by weight, Lintner starch which was added, compensating for the addition by reducing the granular anhydrous sodium tripolyphosphate content. The results are reported in Table 1 in terms of the percent of initial amylase activity at each weekly interval. The initial amylase activity for each composition is also reported on the basis that the α -amylase had an activity of 300,000 units per gram.

TABLE 1

Week	Control				
	Amylase activity, units/gram	Percent α -amylase activity remaining	2%	4%	6%
			Percent α -amylase activity remaining ¹		
0	162.0	100	100 (90)	100 (125)	100 (108)
1	91.3	57	93	85	86
2	38.9	24	49	64	74
3	34.0	21	49	51	61
4	14.5	9	18	19	37
6	6.5	4	20	22	18

¹ Original amylase activity shown in parentheses.

11

The results in Table 1 show that stabilizing effect of water soluble Lintner starch on α -amylase in granular detergent compositions when these compositions are subjected to the stated storage conditions. The effect is most pronounced at the end of the three week storage period. Under more favorable storage conditions (for example, those conditions encountered in the actual marketing of these detergent compositions), these results can be easily translated to more prolonged periods.

EXAMPLE II

Granular detergent compositions were prepared in the manner described in Example I except that 2%, by weight of the enzyme carrier granules, of the starches identified in Table 2 were substituted for the Lintner starch in Example I. A control detergent which was the same as the starch containing detergent compositions but for the absence of added starch was also prepared. Each detergent composition was packed in conventional moisture barrier cartons and stored at 90° F. and 80% relative humidity for seven weeks. The α -amylase activity in the detergent composition was determined after the first, second, fourth and seventh weeks; the percentage of the original α -amylase activity remaining after each period of storage is reported in Table 2. The original amylase activity for each composition is shown in parentheses.

TABLE 2

Control	Soluble starch ¹	Analar soluble starch	Potato starch	Maize starch	Rice starch	Wheat starch
100(143) ²	100 (144)	100 (139)	100 (147)	100 (150)	100 (140)	100 (152)
51-----	65	66	56	66	71	72
32-----	38	48	46	42	40	51
17-----	28	30	26	27	34	32
2-----	14	16	10	10	(9)	16

¹ Obtained from British drug houses.

² Estimated.

³ Not determined.

It is apparent from Table 2 that natural starches from any source and soluble starches (i.e., starches which have been modified to make them more water soluble) prolong the activity of α -amylase in granular detergent compositions.

EXAMPLE III

WSP-X-1000 protein obtained from Wilson Chemical Specialties Co. (U.S.A.) (a powdered, collagen-derived protein having no gelling properties and an average molecular weight of about 10,000) was incorporated in the enzyme carrier granules of Example I in equal weight proportions with Lintner starch. The collagen was added to the granules to stabilize the protease enzymes in the detergent compositions. The detergent compositions were packed in conventional moisture barrier cartons and stored for a period of six weeks at 90° F. and 80% relative humidity. The percentage of the original protease and α -amylase activity in each composition was determined at the end of each week for the first four weeks and at the end of the sixth week.

For comparative purposes, a control detergent which contained no Lintner starch or collagen was prepared and stored under the same conditions.

The proteolytic enzyme activity in the detergent compositions was determined by the casein assay method which is described in B. Hagikara et al.: J. Biochem. (Tokyo) 45, 185 (1958); M. Kunitz, J. Gen. Physiol., 30, 291 (1947); and U.S. SN 721,081 filed Apr. 12, 1968.

The effect of collagen on the storage stabilization of proteolytic enzymes in granular detergent compositions is fully and completely described in Belgian Pat. 724,567; these results were borne out in the present test. At the end of the six weeks' storage tests, the control detergent without collagen contained 48% of its original protease activity; however, the composition containing 1% by weight of the enzyme carrier granules of collagen (and an equal amount of starch) had 83% of its original protease

12

activity. Similarly, those compositions containing 2% collagen and 2% starch; 3% collagen and 3% starch; and 4% collagen and 4% starch; contained 88%, 85% and 80% respectively, of their original protease activity.

The results of the α -amylase activity remaining in these compositions at the end of each weekly storage period (except the fifth week when no determinations were made) are reported in Table 3. The original amylase activity for each composition is shown in parentheses.

TABLE 3.—GELATIN/STARCH CONTAINING COMPOSITIONS

Week	Control	1/1%	2/2%	3/3%	4/4%
0-----	100 (162)	100 (163)	100 (166)	100 (163)	100 (150)
1-----	57	75	82	100	99
2-----	24	62	58	66	70
3-----	21	32	28	40	60
4-----	9	10	8	10	26
6-----	4	9	9	13	12

EXAMPLE IV

Enzyme carrier granules were prepared in the manner described in Example I except that 10% of dextrin was substituted for the Lintner starch. 2% collagen (WSP-X-1000) was also included in the carrier granules. These granules were mixed with spray-dried detergent granules and sodium perborate as described in Example I and

stored in standard moisture barrier cartons at 90° F. and 80% relative humidity for six weeks. The percentage of the original protease activity and α -amylase activity in these compositions was determined after each of the first four weeks of storage and again after the sixth week of storage. The results are reported in Table 4 in which the α -amylase activity in a control detergent containing no dextrin or collagen (but otherwise identical) is also recorded. The original amylase activity for the control and for the composition containing dextrin and collagen is reported in parentheses.

TABLE 4

Percent of original α -amylase activity		
Week	Control	Composition containing dextrin and collagen
0-----	100 (162)	100 (179)
1-----	57	90
2-----	24	72
3-----	21	50
4-----	9	36
6-----	4	38

These results demonstrate the stabilizing effect of dextrin on α -amylase activity in granular detergent compositions under the stated conditions of storage. This effect can be observed (as shown in this example) when dextrin is used in combination with a protease enzyme stabilizing amount of collagen.

What I claim is:

1. A granular detergent composition consisting essentially of, by weight:

(1) from 40% to 98% of a mixture of

(a) an organic detergent selected from the group consisting of soap, anionic synthetic detergents, nonionic synthetic detergents, zwitterionic syn-

13

thetic detergents, ampholytic synthetic detergents, and mixtures thereof, and

(b) an alkaline builder salt selected from the group consisting of inorganic alkaline builder salts, organic alkaline builder salts, and mixtures of inorganic and organic builder salts, in a weight ratio of said organic detergent to said alkaline builder salt of from 1:30 to 4:1;

(2) from 0 to 50% of a sodium perborate bleaching compound;

(3) from 0.0005 to 3% of α -amylase (calculated on the basis of pure α -amylase); and

(4) an α -amylase-stabilizing amount of starch constituting not more than 10% by weight of the composition (in addition to any starch which is an inert carrier for the α -amylase) in a weight ratio ratio of starch to pure α -amylase of from 1:1 to 5000:1.

2. A composition according to claim 1 in which the weight ratio of starch to pure α -amylase is from 8:1 to 460:1.

3. A composition according to claim 1 in which the starch constitutes not more than 6% by weight of the composition.

4. A composition according to claim 1 in which the starch is a granular starch which is a natural starch selected from the group consisting of corn starch, potato starch, wheat starch, tapioca starch, rice starch, waxy maize starch and sweet potato starch.

5. A composition according to claim 1 in which the starch is a modified starch which is a natural starch oxidized by heating or hydrolyzed with an acid or enzyme.

6. A composition according to claim 1 in which the starch is selected from the group consisting of Lintner water-soluble starch, Zulkowsky starch and dextrin.

7. A composition according to claim 1 which the α -amylase is one obtained from *Bacillus subtilis*.

14

8. A composition according to claim 1 containing from 5-40% by weight of the sodium perborate bleaching compound.

9. A composition according to claim 1 in which the weight ratio of organic detergent to alkaline builder salt is from 1:9 to 1:1.

10. A composition according to claim 8 containing the perborate bleaching compound which is sodium perborate tetrahydrate or sodium perborate monohydrate.

11. In a process for producing a granular detergent composition of claim 1 containing enzyme carrier granules which comprises:

(a) preparing a slurry containing an α -amylase enzyme and water; and

(b) spraying said slurry onto partially-hydrated granular sodium tripolyphosphate to form enzyme carrier granules, and

(c) mixing the resultant enzyme carrier granules with the other ingredients of the composition,

the improvement which comprises adding starch to said slurry in an amount which constitutes not more than 10% by weight of the final granular detergent composition.

References Cited

UNITED STATES PATENTS

3,451,935 6/1969 Roald et al. 252-89
3,436,309 4/1969 Ottinger et al. 252-89 X

FOREIGN PATENTS

234,081 12/1944 Switzerland 252-Dig 12

MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252-Dig 12; 195-31 R, 63