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ENZYME-CONTAINING, GRANULAR DETERGENT COMPOSITION

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ABSTRACT OF THE DISCLOSURE

Alkaline, granular detergent composition containing from about 0.5% to about 20% of enzyme carrier granules, said enzyme carrier granules comprising phosphate builder salts, an acid component selected from the group consisting of dihydrogen disodium pyrophosphate, sodium bicarbonate, sodium bisulfate and mixtures thereof, and alkaline proteases or mixtures of alkaline proteases α-amylases.

This application is a continuation-in-part of U.S. patent application, Ser. No. 691,205 filed Dec. 18, 1967, now abandoned in the names of Jerry Edison Davis and Howard John Wick entitled "Enzyme-Containing, Granular Detergent Composition."

FIELD OF THE INVENTION

This invention relates to an alkaline, granular detergent composition suitable for use as a laundry detergent containing from about 0.5% to about 20% of enzyme carrier granules. The enzyme carrier granules comprise phosphate builder salts, an acid component, and alkaline proteases or mixtures of alkaline proteases and α-amylases. The enzyme carrier granules stabilize alkaline proteases or mixtures of alkaline proteases and α-amylases when these enzymes are utilized in conjunction with alkaline, granular detergent compositions.

PRIOR ART

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

In early attempts to utilize enzymes in combination with detergent compositions, the enzymes were merely mechanically mixed into the detergent composition. These enzyme-containing detergent compositions were quite useful if used immediately after being manufactured. However, if these compositions were stored for long periods of time, the enzymes were degraded and/or deactivated in the packaged product. It was found that enzyme stability could be increased by attaching the enzymes to hydratable salts or by conglutinating enzymes and detergent components with a low-melting, ordinarily solid, nonionic detergent. These methods of increasing enzyme stability in detergent compositions are documented in the copending United States patent applications of Roald and de Oude, "Granular Enzyme-Containing Laundry Compositions," Ser. No. 630,199, filed Apr. 12, 1967 now U.S. Pat. 3,451,439, (hereinafter cited as Roald et al.) and McCarty, "Enzyme-Containing Detergent Compositions and A Process for Conglutination of Enzymes and Detergent Compositions," Ser. No. 635,293, filed Apr. 12, 1967, now U.S. Patent 3,519,570 (hereinafter cited as McCarty).

Although the methods of increasing enzyme stability

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documented in McCarty and Roald et al. represented significant advances in the art, further improvements in stabilizing enzymes in detergent compositions were necessary, especially in hot, humid climates.

SUMMARY OF THE INVENTION

When the enzyme carrier granules containing alkaline proteases or mixtures of alkaline proteases and α-amylases are utilized in combination with alkaline detergent granules, the stability of the enzymes is markedly improved when compared with the stability of enzymes incorporated into alkaline, granular detergent compositions by methods known in the prior art.

The enzyme-containing, granular detergent composition of this invention comprises, by weight of the granular detergent composition:

(a) From about 80% to about 99.5% of detergent granules having a pH in aqueous solution at a concentration of about 0.12% by weight ranging from about 8.5 to about 11 and comprising alkaline builder salts and organic detergents, the ratio of alkaline builder salts to organic detergents ranging from about 30:1 to about 1:4;

(b) From about 0.5% to about 20% of enzyme carrier granules having a pH in saturated aqueous solution ranging from about 5.0 to about 7.5 and comprising, by weight of the enzyme carrier granules:

(1) from about 30% to about 75% of sodium tripolyphosphate or mixtures of sodium tripolyphosphate and sodium pyrophosphate;
(2) from about 5% to about 50% of an acid component, i.e., dihydrogen disodium pyrophosphate, sodium bisulfate, sodium bicarbonate, or mixtures thereof;
(3) from 0% to about 20% of anionic synthetic detergents of the sulfate or sulfonate types, preferably sodium alkyl benzene sulfonate, sodium alkyl sulfate, or mixtures thereof, wherein the alkyl group is of branched or straight chain configuration and contains from about 10 to about 18 carbon atoms;
(4) from about 1.5% to about 17% water;
(5) from about 0.001% to about 10% of alkaline proteases or mixtures of alkaline proteases and α-amylases.

This invention is particularly designed to increase the storage life or stability of alkaline proteases or mixtures of alkaline proteases and α-amylases in alkaline, granular detergent compositions. The crux of this invention is the discovery that the addition of an acid component to the enzyme carrier granules markedly improves the stability of alkaline proteases or mixtures of alkaline proteases and α-amylases in an alkaline, granular detergent composition, yet does not sufficiently lower the pH of the alkaline, granular detergent composition in aqueous solution to retard its washing efficacy.

DETAILS AND DESCRIPTION OF THE INVENTION

The bulk of the detergent composition of this invention, i.e., from 80% to about 99.5%, 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 9:1 to about 1:1. They are preferably employed in an amount of from 80% to about 98%.

The alkaline builder salts used herein can be inorganic or organic in nature and can be selected from a wide variety of known 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 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, hydroxymethanediphosphonic acid, carbonyldiphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,3,3-tetraphosphonic acid, propane-1,1,2,3-tetraphosphonic acid, and propane-1,2,2,3-tetraphosphonic acid.

Examples of the above polyphosphonic compounds are disclosed in U.S. Pats. 3,159,581 and 3,213,030 and U.S. patent applications, Ser. No. 266,055, filed Mar. 18, 1963, now U.S. Pat. 3,422,021; Ser. No. 367,419, now abandoned, filed May 18, 1964; Ser. No. 517,073, filed Dec. 28, 1965, now U.S. Pat. 3,422,137; Ser. No. 507,662, filed Nov. 15, 1965, now U.S. Pat. 3,400,176; and Ser. No. 489,637, filed Sept. 23, 1965, 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)-nitrilodiacetic acid, diethylenetriaminepentaacetic acid, 1,2-diaminocyclohexanetetraacetic acid and nitrilotriacetic acid. The trisodium salts of the above acids are generally and preferably utilized herein.

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

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

$$\left[\begin{array}{cc} X & Z \\ | & | \\ -C- & -C- \\ | & | \\ Y & COOH \end{array}\right]_n$$

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:

$$\left[\left(\begin{array}{cc} R & R \\ | & | \\ -C- & -C- \\ | & | \\ H & R \end{array}\right)_{(1-m)}\left(\begin{array}{cc} X & Z \\ | & | \\ -C- & -C- \\ | & | \\ Y & COOH \end{array}\right)_m\right]_n$$

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 alkaline builder salts can be utilized to advantage in this invention.

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

The detergent granules comprising this portion of the detergent composition of this invention can also contain any of the usual detergent adjuvants, diluents, and additives. For example, perfumes, anti-tarnishing agents, inert salts such as sodium sulfate, anti-redeposition agents, bacteriostatic agents, dyes, fluorescers, suds builders, suds depressors, and the like, can be utilized herein without detracting from the advantageous properties of this composition. An enzyme stabilizing advantage for the enzyme carrier granules can also be shown in detergents containing oxygen bleaches such as sodium perborate.

The detergent granules utilized herein are preferably formed by the well-known spray-drying process. However, agglomerated granules can be utilized herein. The particle sizes of the granules should range from about 0.1 mm. to about 1.5 mm. and the densities should range from about 0.2 to about 0.8 gms./cc. to avoid segregation in the finished detergent composition.

To obtain optimum cleaning results, the pH of an aqueous solution containing 0.12% by weight of the above-described detergent granules (ordinary washing concentrations) should range from about 8.5 to about 11.0, preferably from 9.2 to 10.2.

The remaining 0.5% to 20% of the granular detergent composition of this invention is comprised of special enzyme carrier granules. An amount of about 2% to about 20% is preferred, especially about 2% to about 12%. These enzyme carrier granules having a pH in saturated aqueous solution ranging from about 5.0 to about 7.5 are comprised of, by weight of the enzyme carrier granules:

(a) From about 30% to about 75% of phosphate builder salts selected from the group consisting of sodium tripolyphosphate and mixtures of sodium tripolyphosphate and sodium pyrophosphate;

(b) From 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;

(c) From 0% to about 20% of anionic synthetic organic detergents of the sulfate or sulfonate type, preferably sodium alkyl benzene sulfonate, sodium alkyl sulfate, or mixtures thereof, wherein the alkyl group is of branched or straight chain configuration and contains from about 10 to about 18 carbon atoms;

(d) From about 1.5% to about 17% water;

(e) From about 0.001% to about 10% of enzymes selected from the group consisting of alkaline proteases and mixtures of alkaline proteases and α-amylases.

The enzyme carrier granules utilized herein are specially formulated to have the same size and density characteristics as the bulk of the detergent granules to inhibit segregation of the enzymes in the packaged detergent composition. 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. These enzyme carrier granules are also partially effective in controlling free moisture and the relative humidity in the packaged detergent composition. The primary purpose of these enzyme carrier granules, however, is to increase the stability of alkaline proteases and mixtures of alkaline proteases and α-amylases and thus, maintain the cleaning potential of the enzyme-containing granular detergent composition. As used herein, enzyme activity refers to the ability of an enzyme to perform the desired function of soil attack and enzyme stability refers to the ability of an enzyme to remain in an active state, i.e., not to be degraded and/or deactivated.

These granules can advantageously be prepared by different methods, e.g., spray-drying or coagglomeration. The most preferred method of obtaining granules containing the above components is spray-drying. In this method, sodium tripolyphosphate or mixtures of sodium tripolyphosphate and sodium pyrophosphate, the acid component, the anionic synthetic organic detergent, e.g., sodium alkyl benzene sulfonate, sodium alkyl sulfate or mixtures thereof, and water are slurried and this slurry is then spray-dried to a moisture content of from about 1.5% to about 7%, preferably from 1.5% to 4%. An aqueous slurry of alkaline proteases or alkaline proteases and α-amylases is then prepared and this slurry is sprayed onto the enzyme carrier granules. The water in the enzyme-water slurry is bound as water of hydration to the enzyme carrier granules and the enzymes are attached to the enzyme carrier granules.

Another method of preparing the enzyme carrier granules of this invention is by coagglomeration. In this procedure, the various detergent ingredients, i.e., sodium tripolyphosphate, the acid component, the anionic synthetic organic detergent, and the enzymes are sprayed with water and formed into agglomerates in a cement mixer, pan agglomerator or the like. The agglomerates so formed, i.e., enzyme carrier granules, are approximately the same size and density as those utilized in the bulk of the detergent composition.

The alkaline proteases and mixtures of alkaline proteases and α-amylases incorporated into the enzyme carrier granules as above described are significantly stabilized in alkaline detergent compositions when compared with the stability of these enzymes in detergent compositions not containing an acid component in the enzyme carrier granules or in close proximity to the enzymes.

Phosphate builder salts selected from the group consisting of sodium tripolyphosphate and mixtures of sodium tripolyphosphate and sodium pyrophosphate are one of the major components of the enzyme carrier granules and are utilized herein in amounts ranging from about 30% to about 75% by weight of the enzyme carrier granules and preferably in amounts ranging from about 40% to about 65%. The preferred phosphate builder salt is sodium tripolyphosphate.

Mixtures of the sodium salts of tripolyphosphoric acid and pyrophosphoric acid, whether formed by heat degradation of sodium tripolyphosphate or by mixing the two phosphate builder salts, can contain up to 100% sodium tripolyphosphate and not more than about 45% sodium pyrophosphate. Preferably, the amount of sodium pyrophosphate does not exceed about 25% and is usually present in heat-dried sodium tripolyphosphate in amounts in excess of about 5%. Sodium pyrophosphate, sodium orthophosphate or other of the usual heat degradation products of sodium tripolyphosphate are not sufficiently acid to serve as the enzyme stabilizing acid component of the enzyme carrier granules.

Sodium tripolyphosphate is a valuable component of the enzyme carrier granules and provides alkaline builder characteristics and bulk to these granules. This salt is especially valuable herein because in its anhydrous or partially hydrated form it acts as a moisture sink or desiccant and thus controls, to some extent, free moisture in the packaged detergent composition. Therefore, it is preferred that the sodium tripolyphosphate be utilized herein in its anhydrous or partially hydrated form.

Another major component of the enzyme carrier granules is an acid component selected from the group consisting of dihydrogen disodium pyrophosphate, sodium bicarbonate, and sodium bisulfate, or mixtures thereof. This acid component is utilized in the detergent composition of this invention in amounts ranging from about 5% to about 50% by weight of the enzyme carrier granules. The range of about 5% to about 50% provides desirable stabilization, about 10% to about 30% being especially preferred. The preferred acid component is disodium dihydrogen pyrophosphate because, in addition to its acidifying nature, this component, when ionized, is a sequestrant for heavy metal ions.

The acid component is primarily responsible for the enzyme stabilizing effect of these enzyme carrier granules. While the exact mechanism of this enzyme stabilizing effect is not known with certainty, it is believed that free moisture in the packaged detergent composition is saturated or super-saturated with the alkaline builder components. Therefore, localized free moisture (micro-solutions) in the packaged detergent composition may have a pH ranging from about 8.5 to about 13. It is believed that these highly alkaline micro-solutions migrate throughout the packaged detergent composition. The highly alkaline micro-solutions, when in contact with alkaline proteases or mixtures of alkaline proteases and α-amylases, encourage degradation and/or deactivation of the enzymes. However, when an acid component is utilized in conjunction with the enzymes in an enzyme carrier granule, the acid component lowers the pH of the migrating, highly alkaline micro-solutions in close proximity to the enzymes and thus decreases deactivation and/or degradation of the enzymes. As the acid component is utilized sparingly in the enzyme carrier granule and the enzyme carrier granules comprise only a minor portion of the total detergent composition, the pH of a washing solution containing the detergent composition of this invention is not significantly lowered with the concomitant lowered cleaning efficacy. Thus, the enzymes are stabilized in the packaged detergent composition of this invention yet are active in the washing solution and increase the overall cleaning effectiveness of the detergent composition.

It has been found quite surprisingly that the enzyme-stabilizing effect of the hereinbefore described acid component is enhanced by the presence of the hereinbefore described phosphate builder salt. The presence of both the acid component and phosphate builder salt in the enzyme carrier granules of the invention results in a greater level of enzyme stabilization than can be obtained by the employment of either component alone. In addition, the presence in the enzyme carrier granules of the essential phosphate builder salt minimizes the discoloration which often results from the action of the acid component on the optional organic detergent component. Whereas the employment of dihydrogen disodium pyrophosphate, for example, in enzyme carrier granules containing anionic organic detergent and no phosphate builder salt tend to discolor, particularly at elevated temperatures, the employment of a phosphate builder salt such as sodium tripolyphosphate tends to minimize this effect.

While the precise theory or mechanism of the enhanced enzyme stabilization of a combination of acidic component, e.g. dihydrogen disodium pyrophosphate, and phosphate builder salt, e.g. sodium tripolyphosphate, is not completely understood, it is believed that the desirable level of enzyme stabilization is the result, at least in part, of the interaction of such components with moisture in the enzyme carrier granule. It is believed that moisture present in the enzyme carrier granule brings about the formation of hydrated species having lower heats of hydration than the hydrates of the respective phosphate salts. The lesser amount of dissipated heat energy attending the formation of these hydrated species is believed to exert a less harmful effect on the enzyme component than the heat energy accompanying the formation of either hydrate alone.

The enzyme carrier granules of the invention can optionally contain an anionic synthetic organic detergent to minimize undesirable product dustiness (a large portion of very fine particles) and to enhance the washing capabilities of the detergent compositions of the invention. The synthetic organic detergent is preferably sodium alkyl benzene sulfonate, sodium alkyl sulfate or mixtures thereof, wherein the alkyl group is of branched or straight chain configuration and contains from about 10 to about 18 carbon atoms.

Specific examples of the 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 hexadecyl sulfate, sodium octadecyl sulfate, and sodium tetradecyl sulfate. Other examples of anionic synthetic detergents are found in Perry, U.S. Pat. 3,354,092 issued Nov. 21, 1967, at column 3, lines 9 through 43.

As described hereinbefore, the presence of phosphate builder salt, e.g., sodium tripolyphosphate, in the acidulated enzyme carrier granules of the invention makes possible the incorporation of the synthetic organic detergent to enhance cleaning, minimize dustiness and without adverse discoloration. In a preferred embodiment of the invention from about 5% to about 20% of synthetic anionic detergent is employed in the enzyme carrier granules. The anionic detergent can be incorporated by conventional agglomeration methods or preferably by a spray-drying process. Other materials which provide stickiness and thereby minimize dustiness can be employed to advantage.

The fourth component of the enzyme carrier granules is water. Water is utilized in amounts ranging from about 1.5% to about 17% in these granules and preferably in conjunction with the organic detergents to minimize dustiness. The amount of water in the enzyme carrier granules will vary depending upon whether the enzyme carrier granule is prepared by a spray-drying or coagglomeration method. Those prepared by a spray-drying process will contain after incorporation of enzyme an amount of water of about 1.5% to about 10% and preferably about 1.5% to about 7%. Especially preferred is an amount of water of about 1.5% to about 4%. Enzyme carrier granules prepared by a coagglomeration method can contain a greater amount of water corresponding to about 1.5% to about 17% and preferably about 12% to about 15% of the enzyme carrier granule. No more than about 17% water should be utilized in these granules. If more than about 17% water is utilized in these enzyme carrier granules, the desiccant effect of the sodium tripolyphosphate is alleviated and the formation of highly alkaline micro-solutions in close proximity to the enzyme is encouraged. The combination of these two effects can cause severe degradation and/or deactivation of the enzymes in the packaged detergent composition.

The final components of the enzyme carrier granules are enzymes selected from the group consisting of alkaline proteases or mixtures of alkaline proteases and α-amylases. These enzymes are utilized in the enzyme carrier granules in amounts ranging from about 0.001% to about 10% by weight of the enzyme carrier granules and preferably in amounts ranging from about 0.01% to about 5% by weight of the enzyme carrier granules. The alkaline proteases suitable for use herein are those proteases which show optimum activity in enzymatic cleaning, e.g., degradation of protein soil, in aqueous solution at pH's ranging from about 7.8 to about 12 and at temperatures ranging from about 50° F. to about 140° F. For a more complete discussion of enzymes in general, and proteases in particular, see McCarty at pages 5 through 14 now U.S. Pat. 3,519,570, columns 3 through 6. This disclosure is incorporated by reference.

The preferred alkaline proteases for use herein are those alkaline proteases derived from *Bacillus subtilis* which have an optimum activity in the pH range of from 7.8 to 11 and preferably from about 8.2 to about 10 and which are active at temperatures ranging from about 50° F. to about 140° F. These *Bacillus subtilis* derived alkaline proteases are generically, subtilisins. Specific examples of subtilisins useful herein are BPN' and Carlsberg strains. The amino acid sequence of these particular subtilisins, BPN' and Carlsberg, 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, December 25, 1966, at page 5974. (The above description of the amino acid sequence of BPN' and Carlsberg subtilisins is hereby incorporated by reference.)

These alkaline proteases are particularly effective in degrading protein soil in water or an aqueous detergent solution having a pH ranging from about 7.8 to about 12. The proteases catalyze the hydrolysis of the peptide linkage of proteins, polypeptides, and related compounds. Free amino and carboxy groups are thus obtained and the long protein structures of the protein soil are reduced to several shorter chains. These shorter chains can easily be removed from their environment with water or aqueous detergent compositions.

The above described enzymes can be utilized herein in pure form. Generally, however, powdered commercial enzyme compositions containing these enzymes are utilized herein. Thes commercial compositions contain from about 2% to about 80% active enzymes in combination with inert powdered vehicles which may comprise sodium or calcium sulfate as the remaining 20% to 98%. The active enzyme content of these commercial enzyme compositions is the result of manufacturing methods employed and is not critical herein as long as the enzyme carrier granule contains the specified enzyme content.

Specific examples of alkaline proteases suitable for use herein which are sold on a commercial basis are Alcalase (6% subtilisin—Carlsberg strain), Novo Industri, A/S, Copenhagen, Denmark; Monsanto CRD Protease (DA–10) (about 20% subtilisin), Monsanto Company, St. Louis, Missouri; Maxatase (subtilisin) Koninklijke Nederlandsche Gist-En Spiritusfabriek N.V., Delft, Netherlands; Rapidase P–2000, Rapidase, Seclin, France; Biophase (BPN'), Nagase & Co., Ltd., Osaka, Japan. Alcalase, CRD–Protease and Biophase are more specifically described in copending United States patent application, McCarty, "Stabilized Aqueous Enzyme Preparation", Ser. No. 683,196, filed Nov. 15, 1967.

α-Amylases are stabilized by the enzyme carrier granules when utilized in combination with the alkaline proteases. All of the α-amylases show optimum activity in the acid range and are particularly well suited for breaking down starch molecules as they attack the $\alpha_{1,4}$-glycosidic linkages in starch. The remaining shorter chains are, again, easily removed with water or aqueous solutions of detergents. The α-amylases can be obtained from a number of sources, such as animals, cereal grains, bacterial, and fungal sources. Commercial α-amylase compositions can be utilized herein and these compositions include Wallerstein Bacterial α-Amylase, Lot No. 4546A, Wallerstein Company, Staten Island, N.Y.; α-Amylase, Miles Chemical Company, Elkhart, Indiana, the α-Amylase which is an integral part of Monsanto's CRD-Protease (DA–10) (derived from *Bacillus subtilis*); and α-Amylase, Midwest Biochemical Company, Milwaukee, Wis. The α-amylase is used in combination with the alkaline protease in amounts in a weight ratio of alkaline protease to α-amylase of from about 50:1 to about 1:5.

After the enzyme carriers granules are formed as above described, they are simply dry-mixed with the hereinbefore described detergent granules. The enzyme carrier granules are utilized in the detergent composition of this invention in amounts ranging from about 0.5% to about 20%. Preferably from about 2% to about 20% by weight of the total detergent composition of these granules are employed. Especially suitable is an amount of about 2% to about 12%.

By utilizing these enzyme carrier granules, the stability of the alkaline proteases and mixtures of alkaline proteases and α-amylases in the detergent composition is enhanced and the optimum pH range of the detergent composition in aqueous solution is not significantly altered. The enzyme carrier granules can be dyed to give the detergent composition of this invention a distinctive appearance, i.e., speckled, if desired.

Examples

The following examples merely serve to illustrate the invention in specific detail and when read in conjunction with the foregoing description will aid in determining the full scope of the present invention. The examples are merely illustrative and are not intended to restrict this invention. All parts, percentages, and ratios set forth herein, in the preceding specification, and in the appended claims are by weight unless otherwise indicated.

Example I

Enzyme carrier granules were prepared by mixing the following ingredients into a detergent slurry.

Ingredient:	Parts by weight
Anionic organic detergent paste [1]	36.17
Sodium tripolyphosphate	55.00
Dihydrogen disodium pyrophosphate	15.03
Water	28.22
Sodium sulfate	4.55
Total	138.97

[1] The organic detergent paste contained in parts by weight: 5.06 parts sodium tallow alkyl sulfate; 4.14 parts sodium linear alkyl benzene sulfonate having an alkyl chain length distribution of 16% C_{11}, 27% C_{12}, 35% C_{13}, and 22% C_{14}; 6.16 parts sodium sulfate; and 20.81 parts water.

This slurry was mixed until it was homogeneous after which the slurry was spray-dried to a total moisture content of 3.88%. 93.39 parts of enzyme carrier granules were obtained.

When this slurry was spray-dried, a portion of the sodium tripolyphosphate was degraded. The final distribution of phosphate salts on the basis of the original sodium tripolyphosphate added was 75.5% sodium tripolyphosphate; 21.4% sodium pyrophosphate and 3.1% sodium orthophosphate. These phosphate salts were partially hydrated.

Two parts of Alcalase (6% subtilisin), 1.33 parts Monsanto CRD-Protease (DA–10) (reported to be about 20% subtilisin and 14% α-amylase), and 3.33 parts water were slurried together and sprayed onto the 93.39 parts of enzyme carrier granules obtained above. The water was bound as water of hydration by the sodium tripolyphosphate and the enzymes were attached to the enzyme carrier granules. The pH of these enzyme carrier granules in saturated aqueous solution was 6.8. Ten parts of these enzyme carrier granules were mixed with 90 parts of spray-dried detergent granules which had a pH of about 9.2 in aqueous solution at a concentration of 0.12% by weight and which comprised in parts by weight of the detergent granules:

Ingredient:	Parts by weight
A mixture of 55% sodium tallow alkyl sulfate and 45% sodium linear alkyl benzene sulfonate wherein the alkyl chain distribution is 16% C_{11}, 27% C_{21}, 35% C_{13}, and 22% C_{14}	17.5
Sodium tripolyphosphate	50.0
Sodium silicate having an SiO_2:Na_2O ratio of 1.8:1	6.0
Coconut fatty acid ammonio amide	2.5
Sodium sulfate	14.0
Water	10.0

This detergent composition comprising 10 parts enzyme carrier granules and 90 parts of detergent granules will be referred to as Composition A.

The addition of the enzyme-stabilizing detergent granules decreased deactivation and/or degradation of enzymes in Composition A as compared with an enzyme-containing detergent composition which did not contain the enzyme carrier granules of this invention. This comparison was run between the detergent composition described above and a similar detergent composition comprising 10 parts of enzyme carrier granules and 90 parts of detergent granules (Composition B). The detergent granules had the same composition as those described above. The enzyme carrier granules had the same composition as the above described enzyme carrier granules except that 15.03 parts of sodium tripolyphosphate were substituted for 15.03 parts of dihydrogen disodium pyrophosphate. When the enzyme carrier granules were spray-dried, the sodium tripolyphosphate was degraded as described on page 21.

These detergent compositions were separately packaged in cardboard containers and stored at 90° F. and 80% relative humidity for 24 days. Enzyme stability was periodically tested as illustrated in the table below.

	Percent remaining enzyme activity [1] after—					
	0 days	3 days	7 days	14 days	20 days	24 days
Composition A	100	100	100	115	110	105
Composition B	100	91	68	45	45	32

[1] Percent remaining enzyme activity was determined by the Azocoll method. The Azocoll method is based on the release of a water-soluble dye from a water-insoluble protein-dye substrate (Azocoll) by a protease. The amount of dye released under carefully controlled conditions is measured spectrophotometrically. Enzyme activity is calculated from the amount of dye released. Enzyme activities of over 100% reflect errors in sampling techniques and the inherent, but minimal, analytical errors in using the Azocoll method.

As can be seen from the above table, enzyme activity in Composition A, the composition of this invention, was maintained at its original level of activity while enzyme activity in Composition B was reduced by nearly 70% in the same time period. α-Amylase activity was determined by the stained swatch method. Starchy stains were removed more completely with Composition A than with Composition B thus indicating a stabilizing effect on the α-amylase in Composition A.

Example II

Detergent compositions were prepared according to the method of Example I except that the proportions of sodium tripolyphosphate (55.00 parts) and dihydrogen disodium pyrophosphate (15.03 parts) employed in Example I in the preparation of spray-dried granules were varied to illustrate the effects on enzyme stability of (1) the employment of either 70 parts sodium tripolyphosphate or dihydrogen disodium pyrophosphate to the exclusion of the other and (2) mixtures thereof. Detergent compositions, described hereinafter as Compositions C to F, were prepared. The proportions in parts by weight of each phosphate employed in the preparation of the spray-dried granules according to the method of Example I were as follows:

	Sodium tripolyphosphate	Dihydrogen disodium pyrophosphate
Composition:		
C	0	70
D	42	28
E	56	14
F	70	0

The enzyme carrier granules, prepared by application of enzyme in the manner described in Example I, were stored in one-half pint jars at temperatures of 100° F., 120° F. and 140° F. for a period of four weeks. Ten parts of the stored enzyme carrier granules were admixed with 90 parts of the spray-dried enzyme-free detergent granules, described in Example I, to provide Compositions C to F which were evaluated for enzymatic activity by the hereinbefore described Azocoll method.

Compositions D and E of the invention exhibited greater retention of initial enzymatic activity than Compositions C or F. The enzyme carrier granules of Composition C were observed to be of increasingly darker coloration as the storage temperature increased. The enzyme carrier granules of Composition C were observed to have a dark brown color after one week at 140° F. The light color of the enzyme carrier granules of the compositions of the invention, Compositions D and E, was essentially unchanged even after four weeks of storage at 140° F.

The Percent Remaining Enzyme Activity of Compositions C through F, was obtained in the manner described above. The following table shows the Percent Remaining Enzyme Activity of Compositions C to F after storage of the enzyme carrier granules for four weeks at 100° F., 120° F. and 140° F.

	Percent remaining enzyme activity at—		
	100° F	120° F	140° F
Composition C	82	60	7
Composition D	93	118	86
Composition E	83	93	93
Composition F	76	88	64

As can be seen from the above table, the presence of minor amounts of sodium acid pyrophosphate in the sodium tripolyphosphate-containing enzyme carrier granules results in the substantial retention of initial enzyme activity (Compositions D, E and F). The employment of sodium acid pyrophosphate in the preparation of enzyme carrier granules to the exclusion of sodium tripolyphosphate results in substantial loss of initial enzyme activity (Composition C).

Example III

The following ingredients are dry-mixed:

Ingredient:	Parts by weight
Sodium alkyl benzene sulfonate derived from tetrapropylene	9.20
Sodium tripolyphosphate	55.00
Dihydrogen disodium pyrophosphate	15.03
Sodium sulfate	10.71
Alcalase (6% subtilisin)	3.33
Total	93.27

6.73 parts water are sprayed onto this mixture and the ingredients are coagglomerated on a pan agglomerator into enzyme carrier granules having a pH in saturated aqueous solution of 6.8.

Ten parts of these enzyme carrier granules are dry-mixed with 90 parts of the detergent granules of Example I. This composition is stored at 90° F. and 80% relative humidity. The subtilisin is stabilized.

Example IV

The following ingredients are dry-mixed:

Ingredient:	Parts by weight
Sodium alkyl benzene sulfonate derived from tetrapropylene	9.20
Sodium tripolyphosphate	55.00
Dihydrogen disodium pyrophosphate	15.03
Sodium sulfate	13.71
Alcalase (6% subtilisin)	3.33
Total	96.27

3.73 parts water are sprayed onto this mixture and the ingredients are coagglomerated on a pan agglomerator into enzyme carrier granules having a pH in saturated aqueous solution of 6.8.

Ten parts of these enzyme carrier granules are dry-mixed with 90 parts of the detergent granules of Example I. This composition is stored at 90° F. and 80% relative humidity. The subtilision is stabilized.

Example V

The following ingredients are dry-mixed:

Ingredient:	Parts by weight
Sodium tripolyphosphate	55.00
Dihydrogen disodium pyrophosphate	15.03
Sodium sulfate	22.91
Alcalase (6% subtilisin)	3.33
Total	96.27

3.73 parts water are sprayed onto this mixture and the ingredients are coagglomerated on a pan agglomerator into enzyme carrier granules having a pH in saturated aqueous solution of 6.8.

Ten parts of these enzyme carrier granules are dry-mixed with 90 parts of the detergent granules of Example I. This composition is stored at 90° F. and 80% relative humidity. The subtilisin is stabilized.

Example VI

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 the sodium tripolyphosphate in the detergent granules (not, however, in the enzyme carrier granules) in that the composition is an effective laundry detergent: sodium, potassium, ammonium, monoethanol ammonium; diethanol ammonium and triethanol ammonium salts of the following acids: ethylenediaminetetraacetic acid; N-(2-hydroxyethyl)-ethylenediaminetriacetic acid; N-(2-hydroxyethyl)-nitrilodiacetic acid; diethylenetriaminepentaacetic acid; nitrilotriacetic acid; ethylene diphosphonic acid; ethane-1-hydroxy-1,1-diphosphonic acid; ethane-1,1,2-triphosphonic acid; ethane-2-carboxyl-1,1-diphosphonic acid, hydroxymethane-diphosphonic acid, carbonyl-diphosphonic acid; ethane-1-hydroxy-1,1,2-triphosphonic acid; ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,3,3-tetraphosphonic acid; propane-1,1,2,3-tetraphosphonic acid; and propane-1,2,2,3-tetraphosphonic acid and potassium tripolyphosphate; and salts of polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid and citraconic acid and copolymers with themselves and/or ethylene and/or acrylic acid in, e.g., 1:1 molar ratios and having molecular weights of 75,000; 100,000; and 125,000 (the copolymers with ethylene and/or acrylic acid having equivalent weights, based on the acid form of 65, 70 and 75); in the form of their sodium, potassium, triethanolammonium, diethanolammonium and monoethanolammonium salts.

Results substantially similar to those obtained in the previous examples are obtained when the following organic detergents are substituted, either wholly or in part, for the sodium alkyl benzene sulfonate or mixtures of sodium alkyl benzene sulfonate and sodium tallow alkyl sulfate in the detergent granules (not, however, in the enzyme carrier granules) in that the composition is an effective laundry detergent: sodium linear dodecyl benzene sulfonate, the condensation product of 1 mole of dodecyl phenol with 15 moles of ethylene oxide, dimethyldodecylamine oxide, dimethyldodecylphosphine oxide, 3-(N,N - dimethyl - N - hexadecylammonio)-2-hydroxypropane-1-sulfonate and sodium-3-dodecylaminopropane sulfonate.

Results substantially similar to those obtained in the previous examples are obtained when the following acid components are substituted in the enzyme carrier granules, either wholly or in part, for the dihydrogen disodium pyrophosphate in that the enzymes are stabilized: sodium bicarbonate, sodium bisulfate, and mixtures of sodium bicarbonate and sodium bisulfate.

Results substantially similar to those obtained in the previous examples are obtained when the following anionic synthetic detergents are substituted, either wholly or in part, for the anionic synthetic detergents utilized in the enzyme carrier granules in that the enzyme carrier granules are not dusty and are of proper size and density: sodium decylbenzene sulfonate, sodium dodecylbenzene sulfonate, sodium tridecylbenzene sulfonate, sodium hexadecylbenzene sulfonate, sodium octadecylbenzene sulfonate, sodium octadecyl sulfate, sodium hexadecyl sulfate, sodium tetradecyl sulfate, and sodium dodecyl sulfate, sodium tetradecene sulfonate, sodium dodecyl glyceryl ether sulfonate, sodium salts of the sulfated reaction product of 1 mole of coconut fatty alcohol and 3 moles of ethylene oxide.

Results substantially similar to those obtained in the previous examples are obtained when the following enzymes are substituted, either wholly or in part, for the α-amylases and alkaline proteases utilized in the previous examples in that these enzymes are stabilized: subtilisin, BPN′, Carlsberg subtilision, Alcalase, Monsanto CRD Protease (DA–10), Maxatase, Rapidase P–2000, Biophase, Wallerstein Bacterial α-amylase Lot No. 4546A, Miles α-amylase, and Midwest Biochemical's α-amylase.

What is claimed is:

1. A granular detergent composition containing built detergent granules in admixture with enzyme carrier granules, said total granular detergent composition consisting essentially of, by weight:

(a) from about 80% to about 99.5% of said built detergent granules having a pH in aqueous solution at a concentration of about 0.12% by weight ranging from about 8.5 to about 11 and consisting essentially of alkaline builder salts and organic detergents, selected from soap, anionic, zwitterionic, nonionic and amphoteric organic detergents the ratio of alkaline builder salts to organic detergents ranging from about 30:1 to about 1:4; and

(b) from about 0.5% to about 20% of enzyme carrier granules having a pH in saturated aqueous solution ranging from about 5.0 to about 7.5 and consisting essentially of by weight of the enzyme carrier granules:

(1) from about 30% to about 75% of phosphate builder salts selected from the group consisting of sodium tripolyphosphate and mixtures of sodium tripolyphosphate and sodium pyrophosphate;

(2) from 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) from 0% to about 20% of anionic synthetic organic sulfonate or sulfate detergent;

(4) from about 1.5% to about 17% water; and

(5) from about 0.001% to about 10% of enzymes selected from the group consisting of alkaline proteases and mixtures of alkaline proteases and α-amylases.

2. The enzyme-containing, granular detergent composition of claim **1** wherein the detergent granules comprise alkaline builder salts and organic detergents in a weight ratio of builder salts to organic detergents ranging from about 9:1 to about 1:1 and having a pH in aqueous solution at a concentration of 0.12% by weight ranging from 9.2 to 10.2 and the anionic synthetic organic detergent of the enzyme carrier granules is present in an amount of about 5 to about 20% and is 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 from about 10 to about 18 carbon atoms.

3. The enzyme-containing, granular detergent composition of claim **2** wherein the enzyme carrier granules comprise from about 2% to about 20% by weight of the total detergent composition.

4. The enzyme-containing, granular detergent composition of claim **3** wherein the enzyme carrier granules comprise from about 2% to about 12% by weight of the total detergent composition.

5. The enzyme-containing, granule detergent composition of claim **4** wherein the enzyme carrier granules comprise from about 40% to about 65% of phosphate builder salts by weight of the enzyme carrier granules.

6. The enzyme-containing, granular detergent composition of claim **5** wherein the phosphate builder salt of the enzyme carrier granules is sodium tripolyphosphate.

7. The enzyme-containing, granular detergent composition of claim **6** wherein the acid component of the enzyme carrier granules is dihydrogen disodium pyrophosphate, said acid component comprising from about 10% to about 30% by weight of the enzyme carrier granules.

8. The enzyme-containing, granular detergent composition of claim **7** wherein the enzyme carrier granules contain from about 1.5% to about 7% water by weight of the enzyme carrier granules.

9. The enzyme-containing, granular detergent composition of claim **8** wherein the enzyme carrier granules contain from about 1.5% to about 4% water by weight of the enzyme carrier granules.

10. The enzyme-containing, granular detergent composition of claim **9** wherein the enzyme carrier granules contain alkaline proteases which have optimum activity in aqueous solution at pH's ranging from about 7.8 to about 12.

11. The enzyme-containing, granular detergent composition of claim **10** wherein the enzyme carrier granules contain from 0.01% to about 5% of enzymes selected from the group consisting of alkaline proteases and mixtures of alkaline proteases and α-amylases wherein the alkaline proteases are derived from *Bacillus subtilus* and have optimum activity in aqueous solution in the pH range of from about 8.2 to about 10.

12. The enzyme-containing, granular detergent composition of claim **11** wherein the alkaline proteases are selected from the group consisting of Carlsberg subtilisin and BPN′ subtilisin.

13. The enzyme-containing, granular detergent composition of claim **12** wherein the enzyme carrier granules contain a mixture of alkaline proteases and α-amylases in a weight ratio of proteases to α-amylase of from about 50:1 to about 1:5.

References Cited

UNITED STATES PATENTS

3,296,094	1/1967	Cayle	195—63
3,451,935	6/1969	Roald et al.	252—135

FOREIGN PATENTS

14,296	1/1958	Germany	252—Dig 12
130,377	1/1936	Germany	252—Dig 12

OTHER REFERENCES

Hoogerheide et al., Kemian Teallisuus, No. 3, 1967, 207–212 and 221.

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