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3,451,935

GRANULAR ENZYME-CONTAINING LAUNDRY COMPOSITION

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U.S. Cl. 252—135

17 Claims

ABSTRACT OF THE DISCLOSURE

Powdered enzymes, which are cleaning aids, are attached to granular carriers which comprise partially-hydrated hydratable salts such as sodium tripolyphosphate. The attachment is done in the presence of water which effects the partial hydration. The granular carrier with the attached enzyme is useful in pre-wash soaking and in conjunction with detergent compositions.

CROSS REFERENCE

This application is a continuation-in-part of copending application Ser. No. 544,705 filed Apr. 25, 1966, now abandoned, and copending application Ser. No. 620,603 filed Mar. 6, 1967, now abandoned.

FIELD OF INVENTION

This invention relates to a laundry composition comprising a powdered enzyme attached to a granular carrier which is based on an hydratable salt. The invention also relates to a method for attaching powdered enzyme to the granular carrier.

PRIOR ART AND PROBLEMS CONNECTED THEREWITH

Laundry products containing enzymes are old. See, for example, U.S. Patent 1,882,270, Frelinghusen, Oct. 11, 1932. Enzymes aid in laundering by attacking soil and stains found on soiled fabrics. Soils and stains are decomposed or altered in such an attack so as to render them more removable during laundering. Enzymes can be used either in a soaking or pre-wash product designed to prepare soiled fabric for more effective detergency when the fabrics are subjected to conventional laundering, or as a component of a detergent formulation containing conventional cleaning ingredients. The enzymes suitable for such laundry uses are usually found in a fine powder form. Enzymes are expensive and powerful materials which must be judiciously formulated and used. Such fine powders of concentrated materials are difficult to handle, difficult to measure and difficult to formulate.

Prior art enzyme-containing laundry products are mechanical mixtures of a fine enzyme powder and other granular materials. Enzyme powder in such mechanical mixtures tends to segregate, resulting in a non-uniform product. Nonuniformity results in an undependable product in use, particularly for measurement purposes. Such mechanical mixtures also present stability problems resulting from the mobility of the enzyme powder in the mixture; it is exposed to some cleaning ingredients and environmental condition which may either attack the enzyme or aid it in degrading itself. For example, moisture tends to cause the enzyme to degrade itself; many enzymes are incompatible with highly alkaline detergent materials such as caustic soda, particularly in the presence of moisture.

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BRIEF SUMMARY OF INVENTION

The granular laundry composition of this invention comprises a powdered enzyme attached to a granular carrier which overcomes the disadvantages associated with the prior art products. The granular carrier comprises a partially-hydrated hydratable salt. The process of this invention is the application of powdered enzyme to such a granular carrier in the presence of water.

DETAILED DESCRIPTION

The enzyme powder is attached to a granular carrier comprising a partially-hydrated hydratable salt having a pH in the range of 4 to 12. The close association involved in such attachment tends to isolate the enzyme powder from other materials used in an enzyme-containing product which might be unfavorable to the enzyme from a stability or activity standpoint. Enzyme activity is its ability to perform the desired function of soil attack. Enzyme stability is its ability to remain in an active state. The attachment of the enzyme powder to the larger carrier granules overcomes segregation problems of the prior art mechanical mixtures.

In the compositions of this invention, the salt employed in or as the granular carrier must be water-soluble and in a hydratable state to achieve the desired physical attachment characteristics and stability advantages. The enzyme powder is attached to the granular carrier in the presence of water, the water usually being used as the vehicle for the enzyme powder while attachment is being effected. The contact of the granular carrier by enzyme powder in the presence of water results in receipt of the water by the hydratable salt in the carrier in such a way that the enzyme powder is drawn on and attached to the surface of the carrier granules in a blotter-like or sponge-like action, leaving dry enzyme powder on the surface of the granules. To the extent that the enzyme applied to the carrier is dissolved in the water, some enzyme can be drawn into the granular carrier and attached therewith as well as thereon.

The water taken up by the granular carrier in the attachment process results in partial hydration of the hydratable salt short of full hydration. The remaining increment of hydratability of the hydratable salt permits any free moisture associated with the laundry composition of the invention, which might otherwise tend to cause degradation of the attached enzyme powder, to be received into the hydratable salt of the granular carrier as additional water of hydration. Water so received is not in contact with the enzyme to an extent significant enough to cause degradation thereof. This provides a much more favorable stability situation for the laundry composition which contains the enzyme and granular carrier.

While modern laundry products and detergent compositions are well packaged, they are often exposed to humidity initially in the package or after the package is opened and the contents are being periodically used. The compositions of this invention have, by virtue of the attachment of the powdered enzyme to the granular carrier, stability characteristics that are markedly superior to the mechanical mixtures of the prior art where the enzyme powder is mobile and exposed.

HYDRATABLE SALTS

Water-soluble hydratable salts employed as or in the granular carrier of the compositions of this invention have certain characteristics relative to pH and hydration characteristics. As used in the specification and claims the term hydratable salt defines one compound of the desired properties or a mixture of such compounds.

Both the granular carrier and the hydratable salt used thereas or therein should provide a pH in water solution

in the range of from 4-12. Carrier granules and hydratable salt having pH values from 4-7 are provided when the particular powdered enzyme chosen for attachment to the granular carrier prefers an acidic environment for optimum activity and stability. Neutral or slightly alkaline pH's of 7-8 are employed for analagous reasons. Granular carrier and hydratable salts providing pH's in the range of 4-8 generally function solely as a carrier for the powdered enzyme. When the granular carrier, and the hydratable salt used therein, function as a detergent or a detergent component in addition to a carrier for the powdered enzyme, materials providing high pH's in the 4-12 range are used, preferably in the range of 8-11. Water-soluble hydratable builder salts, serving as or in a granular carrier as hereinafter described, either in granular form per se or as a portion of a multi-component detergent granule, provide pH's in this preferred range of 8-11.

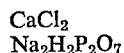
Preferably the hydratable salt and powdered enzyme are matched for pH, that is the inherent pH's of the enzyme and salt are within a pH unit or two. In the composition of this invention, however, such pH matching is not essential since the moisture absorbing capacity of the partially-hydrated hydratable salt keeps the moisture away from the enzyme carrier interface, thereby precluding any pH differential in the salt and enzyme from causing degradation of the enzyme.

The hydratable salt employed as the granular carrier or in the granular carrier should hold its water of hydration tightly and should readily accept more water to fulfill the function required in this invention. Suitable hydratable salts are those having a vapor pressure not greater than about 13.15 mm. of Hg at 20° C. and atmospheric pressure. This vapor pressure corresponds to 75% relative humidity as measured over the hydratable salt at the same conditions. Hydratable salts with lower vapor pressures are preferred. Vapor pressure varies with the compound and with the amount of water of hydration already in the compound. An anhydrous salt has no vapor pressure. In the composition of this invention the hydratable salt will always contain some water of hydration and will have some vapor pressure, depending on how much water was used to effect the attachment of the powdered enzyme to the granular carrier. In the process of this invention either anhydrous or partially-hydrated hydratable salts can be used as a starting material.

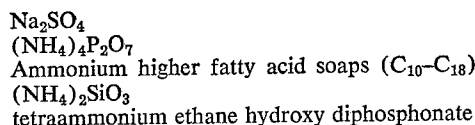
Another important characteristic of the hydratable salt is its capacity to take water of hydration. Preferably this capacity should be in the range of 0.1 to 1.3 lbs. of water per lb. of anhydrous hydratable salt. One pound of anhydrous sodium tripolyphosphate will hydrate about 0.3 pound of water.

Examples of suitable water-soluble hydratable salts for use as or in the granular carrier are as follows.

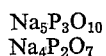
I. Hydratable salts of an acid with a large, and a base with a small, dissociation constant providing a pH of about 4 to about 7.



II. Hydratable salts of an acid and a base with approximately the same dissociation constant having a pH of approximately 7-8



III. Hydratable salts of an acid with a small, and a base with a large, dissociation constant (e.g. builder salts) having a pH of about 8-11 or 12



trisodium methane or ethane hydroxy diphosphonate, trisodium methane or ethane diphosphonate, tetra sodium ethane, triphosphonate, tetra sodium ethane hydroxytriphosphonate, tetra sodium propane tetra, penta or hexaphosphonate

- 5 Na_2CO_3
sodium higher fatty acid soaps (C_{10} - C_{18})
- Na_2SiO_3
- $\text{Na}_2\text{B}_4\text{O}_7$
- 10 Na_2HPO_4
 Na_3PO_4
trisodium nitrilotriacetate
di-, tri- and tetra sodium ethylenediaminetetraacetate

The above list is only exemplary. Many other hydratable salts having the desired pH, vapor pressure and hydration characteristics can be employed. The cations of such hydratable salt can be alkali metal, such as sodium, lithium or potassium, ammonium, alkanolammonium (e.g. triethanolammonium) and alkaline earth metal such as calcium and barium. Mixtures of such salts can be used.

Many of these hydratable salts vary in hydration capacity, holding from 1 to 10 or 12 moles of water.

The preferred hydratable salts are sodium builder salts such as sodium tripolyphosphate, sodium tetraborate, sodium pyrophosphate. These builder salts, in any of their partially hydrated forms have a vapor pressure of less than 13.15 mm. of Hg at 20° C. and one atmosphere. Sodium tripolyphosphate, sodium pyrophosphate and sodium tetraborate have pH's of about 9-10.

With the powdered enzyme attached to the granular carrier, the hydratable salt is preferably not more than 90% hydrated (based on total hydration capability by weight) in order to provide capacity for additional hydration during any exposure of the product to free moisture. Desirably this figure is not more than about 50% of the total hydration capacity. Generally, about 33% hydration of the total hydration capacity of the hydratable salt is effected when the powdered enzyme is attached to the granular carrier.

GRANULAR CARRIER

The hydratable salt can be used either per se as the granular carrier or can comprise a portion of a multi-component granular carrier. The other components of the granular carrier, when the hydratable salt is only a portion thereof, can comprise diluent salts, organic detergents, detergency builder salts not having the necessary hydrate characteristics, and other detergent composition components of the usual type. The granular carrier of this invention ranges in particle size from about .075 mm. to about 3.33 mm. (about .003" to about 1/8"). This size range corresponds to granules which pass through 6 mesh and remain on 200 mesh (Tyler standard screen). A preferred size range is 0.2 mm. to 2 mm. Laundry products, such as conventional spray-dried detergent granules are in these size ranges which are easy to measure and use without dustiness. The granular carrier preferably has a density in the range of from about 0.2 gram/cc. to about 0.8 gram/cc.

The hydratable salts can comprise from 20% to 100% of the granular carrier. Preferably the hydratable salt comprises from 40% to 90% of the granular carrier in order to provide ample hydration capacity for the carrier and to permit inclusion of other desired components in the granular carrier, such as an organic detergent. When an organic detergent is used with the hydratable salt, particularly a hydratable builder salt, the ratio of salt to detergent ranges from 1:4 to 20:1, generally from 1:1 to 9:1. The granular carrier can also contain minor materials: for example corrosion inhibitors such as benzotriazole, antiredeposition agents such as sodium carboxymethyl cellulose, optical brighteners, bactericides, perfumes and dyes. These optional minor components are each commonly used in amounts up to 2 to 5% by weight of the granular carrier.

The granular carrier with the enzyme attached can be used per se as a pre-wash soaking agent or, when the carrier comprises a detergent component such as an hydratable builder salt, as a cleaning agent. The granular carrier with attached enzyme can be admixed with other granular detergent materials of approximately the same particle size and density to form a multi-component, heavy-duty laundry detergent composition tailored to have a number of desirable characteristics. In such a case, the granular carrier with enzyme preferably is in an amount ranging from about 0.2% to about 30% by weight of such a multi-component detergent composition and is uniformly distributed throughout the detergent composition, so that any random sample thereof has about the same formulation as any other sample. Use of less than about 0.2% carrier+enzyme makes uniformity difficult; more than 30% results in a loss of the advantages of such blending, sometimes called master-batching. If desired, the carrier with enzyme granules can be dyed a bright color and admixed with a white or slightly colored granular detergent system to provide an overall composition having a distinctive speckled appearance, in accordance with the teachings of Canadian Patent 577,479, Britt.

Such an admixture, whether or not with a dye, has the advantage of permitting efficient incorporation of enzymes in a multi-component detergent composition wherein the total proportion of granules to be treated with enzyme powder is relatively minor. The laundering advantages of enzymes are achieved with only a minor amount thereof in a detergent composition. Therefore, it is more efficient to blend a minor proportion of granular carrier having a moderate amount of attached enzyme with a major proportion of enzyme-free granules than to attach a very small amount of enzyme to each of the granules in a granular detergent product. Moreover, the granular carrier is designed to provide improved stability whereas the detergent composition may not provide conditions for optimum stability.

In a multi-component detergent composition comprising about 0.2% to about 30% of the granular carrier with attached enzyme, the remaining 70% to 99.8% can be granular detergent materials of the conventional types. Generally such materials are mixtures of builders and organic detergents in weight ratios of 1:4 to 20:1. The builders can be of the hydratable type required for the granular carrier or can be of other types such as the polycarboxylate builder salts of U.S. Patent 3,308,067, Diehl, issued Mar. 7, 1967.

Whether the hydratable salt comprises all or only a portion of any particular granular carrier in the desired size range, it can be in any particulate physical form such as granular anhydrous sodium tripolyphosphate which is relatively dense, or a heat-dried or agglomerated hydratable salt-containing particle which has reduced density and expanded surface area formed as a result of a drying or agglomeration step. Conventional spray-dried synthetic detergent granules can be used since they comprise a significant portion of hydratable salt, particularly builder salt such as sodium tripolyphosphate.

A granular carrier which can be used advantageously comprises spray-dried detergent granules containing sodium tripolyphosphate and anionic organic synthetic detergent in a weight ratio ranging from 8:1 to 2:1, containing less than 4%, and preferably less than 2.5% moisture (water or hydration) and being free from the highly alkaline sodium silicate commonly used in spray-dried synthetic detergent granules.

A low density sodium tetraborate can also be used as a granular carrier. It has an average bulk density of about 0.4 to 0.6 gram per cc. and a moisture (water of hydration) content of less than 4%, preferably less than 2.5%. It is formed by heating sodium borate decahydrate as it passes downward through a chamber containing heated, upwardly-rising air in the neighborhood of 450° to 550° F.

ENZYMES

The enzymes of this invention are solid catalytically active protein materials which degrade or alter one or more types of soil or stains encountered in laundering situations so as to remove the soil or stain from the fabric or object being laundered or make the soil or stain more removable in a subsequent laundering step. Both degradation and alteration improve soil removability. Suitable enzymes are those active at a pH in range of from about 4 to about 12 and preferably in the pH range of from about 7 to about 11 and at a temperature in the range of from about 50° F. to about 185° F., preferably from 70° F. to 170° F.

White, Handler, Smith, Stetten, Principles of Bio-Chemistry (First Edition, 1954), is a valuable reference on enzymes.

Those enzymes which degrade or alter one or more types of soil are large in number and can be grouped into five major classes on the basis of the reactions which they perform in such degradation or alteration. These classes and some of the pertinent sub-classes are described as follows in reaction terms.

I. Enzymes which catalyze the addition or removal of water and thereby degrade soil, especially of a protein type.

A. Hydrolyzing enzymes (hydrolases, e.g., proteases, esterases, carbohydrases and nucleases)

(1) Cleave ester linkages (carboxylic ester hydrolases, phosphoric monoester hydrolases, phosphoric diester hydrolases).

(2) Cleave glycosides (glycosidases).

(3) Cleave peptide linkages (α -aminopeptide amino acid hydrolases, α -carboxypeptide amino acid hydrolases).

B. Hydrating enzymes (hydrases). (Hydrating enzymes can also be classed as oxidoreductases.)

II. Enzymes which catalyze the oxidation or reduction of a substrate (oxidoreductases). These act on oxidizable or reducible soil to degrade it in a manner analogous to an oxidizing bleach or a reducing agent.

A. Act on $>CH-OH$ group of donors (glucose oxidase, alcohol dehydrogenase).

B. Act on the aldehyde or keto-group of donors (xanthine oxidase, glyceraldehyde-3-phosphate dehydrogenase).

C. Act on the $>CH-CH<$ group of donors.

D. Act on the $>CH-NH_2$ group of donors (amino acid oxidases).

III. Enzymes which transfer a radical from one molecule to another (transferases) and alter soil such as hydrocarbon soil (e.g. squalene or sterol) or carbohydrate soil to make it more removable, e.g., by solubilizing it.

A. Transfer a monosaccharide radical (transglycosidases).

B. Transfer a phosphoric acid radical (transphosphorylases and phosphomutases).

C. Transfer an amino group (transaminases).

D. Transfer a methyl group (transmethylases).

E. Transfer an acetyl group (transacetylases).

IV. Enzymes which split or form bonds without group transfer (desmoses) and degrade soil such as hydrocarbon soil (e.g. squalene or sterol) to make it more removable.

A. Enzymes which form C—C bonds, C—O bonds and C—N bonds (ligases).

B. Enzymes which split C—C bonds, C—O bonds and C—N bonds (lyases).

V. Enzymes which isomerize molecules (isomerases) and chemically alter a soil such as lipid and carbohydrate soil to make it more removable, for example by solubilizing.

A. Racemases and epimerases.

B. cis-trans Isomerases.

C. Intramolecular transferases.
D. Intramolecular oxido reductases.

In a few cases a single enzyme may fit more than one of these classes. A number of enzyme reactions are not understood clearly enough that their place in the above classification can be stated.

In summary the hydrolases, hydrases, oxidoreductases and desmolases degrade soil to remove it or make it more removable and the transferases and isomerases alter soil so as to make it more removable. Of these classes the hydrolases are particularly preferred.

The hydrolases catalyze the addition of water to the substrate, i.e., the substance such as soil with which they interact, and thus, generally, cause a breakdown or degradation of such a substrate. This breakdown of the substrate is particularly valuable in the ordinary washing procedures, as the substrate and the soil adhering to said substrate is loosened and thus more easily removed. For this reason, the hydrolases are the most important and most preferred sub-class of enzymes for use in cleaning applications. Particularly preferred hydrolases are the proteases, esterases, carbohydrases and nucleases, with the proteases having the broadest range of soil degradation capability.

The proteases catalyze the hydrolysis of the peptide linkage of proteins, polypeptides and related compounds to free amino and carboxyl groups and thus break down the protein structure in soil. Specific examples of proteases suitable for use in this invention are pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, subtilisin, BPN', papain, bromelin, carboxy peptidase A and B, amino peptidase, aspergillopeptidase A and aspergillopeptidase B. Preferred proteases are serine proteases which are active in the neutral to alkaline pH range and one produced from microorganisms such as bacteria, fungi or mold. The serine proteases which are procured by mammalian systems, e.g., pancreatin, are useful in acid situations.

Esterases catalyze the hydrolysis of an ester, such as lipid soil, to an acid and an alcohol. Specific examples of the esterases are gastric lipase, pancreatic lipase, plant lipases, phospholipases, cholinesterases and phosphotases. Esterases function primarily in acid systems.

Carbohydrases catalyze the breakdown of carbohydrate soil. Specific examples of this class of enzymes are maltase, saccharase, amylases, cellulase, pectinase, lysozyme, α -glycosidase and β -glycosidase. They function primarily in acid to neutral systems.

The nucleases catalyze the breakdown of nucleic acids and related compounds, degrading residual cell soil such as skin flakes. Two specific examples of this subgroup are ribonuclease and deoxyribonuclease.

The enzymes utilized in this invention are generally obtained and stored in a dry, powdered form although they can be utilized in the process of the invention in a water slurry. The dry, powdered form is most easily handled and generally is more stable than enzymes in a water slurry. Enzymes per se have molecular diameters of from about 30 angstroms to several thousand angstroms. However, the particle diameters of the enzyme powder are normally much larger due to agglomeration of individual enzyme molecules or addition of inert vehicles such as organic clays, sodium or calcium sulfate or sodium chloride, during enzyme manufacture. Enzymes are grown in solution. Such vehicles are added after filtration of such solution to precipitate the enzyme in fine form which is then dried; calcium salts also stabilize enzymes. The enzyme plus inert vehicle usually comprise about 2% to about 80% enzyme. The enzyme powders of this invention, including the examples, mostly are fine enough to pass through a Tyler Standard 20 mesh screen (0.85 mm.), although larger agglomerates are often found. Some particles of commercially available enzyme powders are fine enough to pass through a Tyler Standard 100

mesh screen. Generally a major amount of particles will remain on a 150 mesh screen. Thus, the powdered enzymes utilized herein usually range in size from about 1 mm. to 1 micron, and most generally from 0.1 mm. to 0.01 mm. The enzyme powders of the examples have a particle size in these ranges.

The commercial powdered enzyme products are useful and are generally dry powdered products comprised of about 2% to about 80% active enzymes in combination with an inert powdered vehicle such as sodium or calcium sulfate, sodium chloride, clay or starch as the remaining 98-20%. Active enzyme content of a commercial product is a result of manufacturing methods employed and is not critical herein so long as the laundry product has the desired enzymatic activity. Many of these commercial products contain the preferred proteases as the active enzyme. In most cases, a subtilisin comprises the major portion of the proteases: other examples of hydrolases generally included in commercial products are lipases, carbohydrases, esterases and nucleases.

Specific examples of commercial enzyme products include: Alcalase, Maxatase, Protease B-4000 and Protease AP, CRD-Protease, Viokase, Pronase-P, Pronase-AS and Pronase-AF, Rapidase P-2000, Takamine, Bromelain 1:10, HT proteolytic enzyme 200, Enzyme L-W (derived from fungi rather than bacteria), Rhozym P-11 concentrate, Pectinol, Lipase B, Rhozyme PF, Rhozyme J-25; Rhozyme PF and J-25 have salt and corn starch vehicles and are proteases having diastase activity; Amprozyme 200.

CRD Protease (also known as Monsanto DA-10) is a useful powdered enzyme product. CRD-Protease is reported to be obtained by mutation of a *Bacillus subtilis* organism. It is about 80% neutral protease and 20% alkaline protease. The neutral protease has a molecular weight of about 44,000 and contains from 1 to 2 atoms of zinc per molecule. Its particle size ranges predominantly from 0.03 mm. to 0.1 mm. The CRD-Protease can be used in an aqueous system having a pH ranging from about 5.4 to about 8.9. It can be prepared to range in active enzyme content from 20% to 75%. The presence of CaCl_2 in the enzyme powder increases the pH range over which this enzyme can be utilized. This enzyme can be utilized in the composition of this invention with excellent results in washing solutions at temperatures ranging from about 50° F. to about 150° F. and at lower pH's suitable for prewash soaking or higher pH's for detergency purposes.

Pronase-P, Pronase-AS and Pronase-AF are powdered enzyme products which can also be used to advantage in this invention. These enzymes are produced from the culture broth of *Streptomyces griseus* used for streptomycin manufacture. They are isolated by the successive resin column treatment. The major component of the pronase is a neutral protease named as *Streptomyces griseus* protease. This enzyme product contains a calcium stabilizer salt and is fairly stable over a wide pH range, e.g., 4 to 10, and is fairly stable over a temperature range of 50° F. to 150° F.

Another enzyme product preferred for use in the detergent compositions of this invention, including a number of the examples, is a proteolytic enzyme, a serine protease, sold under the trade name of Alcalase. Alcalase is described, in a trade bulletin bearing that name, as a proteolytic enzyme preparation manufactured by submerged fermentation of a special strain of *Bacillus subtilis*. The primary enzyme component of Alcalase is subtilisin. In addition to proteolytic activity, Alcalase exhibits other forms of desirable enzymatic activity. Alcalase is a fine grayish powder having a crystalline active enzyme content of about 6% and a particle size ranging from 1.2 mm. to .01 mm. and smaller, about 75% passing through a 100 mesh Tyler screen. The remainder of the powder is comprised primarily of sodium chloride, calcium sulfate and various inert organic vehicle materials. Alcalase has un-

usually stable properties in solution. For example, Alcalase can withstand a pH of about 9 at relatively high temperatures, i.e., 150–170° F., for a short time. At 120° F., the activity of Alcalase is virtually unchanged in a 24-hour period when held at this pH. Alcalase can be advantageously used with soap and detergent compositions of this invention.

The particular enzyme chosen for use in the products and process of this invention depends on the conditions of final utility, including carrier pH, composition pH, use pH, use temperature and soil types to be degraded or altered. The enzyme can be chosen to provide optimum activity and/or stability for any given set of utility conditions.

The powdered enzymes are attached to the granular carrier in the laundry compositions and process of this invention to provide from about .001% to about 20%, preferably .01% to 5% enzyme of the total weight enzyme powder and carrier. When the carrier with enzyme is uniformly blended with detergent granules to form a detergent composition, the enzyme concentration usually ranges from 0.001% to 2%, generally 0.005% to 0.5% of the detergent composition. Taking into account the inert vehicle in commercial powdered enzyme products, the amount of enzyme products (enzyme+vehicle) attached to the granular carrier can range up to 40%, preferably up to 20%, of the total weight of enzyme plus carrier.

ORGANIC DETERGENTS

The organic detergent compounds which can be utilized as optional components in the compositions of this invention are soap and anionic, nonionic, ampholytic and zwitterionic synthetic detergents and mixtures thereof and are exemplified as follows:

(a) Water-soluble soap: Examples of suitable soaps for use in this invention are the sodium, potassium, ammonium and alkanol ammonium (e.g. triethanolammonium) salts of higher fatty acids containing from about 10 to about 22 carbon atoms. Particularly useful are the sodium and potassium salts of the mixture of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soap.

(b) Anionic synthetic non-soap detergents, a preferred class, can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric 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 the synthetic detergents which form a part of the preferred compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈–C₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, including those of the types described in United States Letters Patent Nos. 2,220,099 and 2,477,383 (the alkyl radical can be a straight or branched aliphatic chain); 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 or 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 salts of alkyl phenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to about 12 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil, sodium or potassium salts of fatty acid

amide of a methyl tauride in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number specifically set forth in United States Letters Patents Numbers 2,486,921, 2,486,922 and 2,396,278. Other important anionic detergents, sulfonated olefins, are described in the copending application of Phillip E. Pflaumer and Adriaan Kessler, Ser. No. 561,397 filed June 29, 1966.

(c) Nonionic synthetic detergents: One class can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Another class has semi-polar characteristics. Preferred classes of nonionic synthetic detergents are as follows:

(1) A class of nonionic synthetic detergents under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water 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.

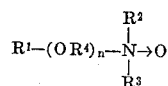
(2) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the said ethylene oxide being present in amounts equal 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) Those nonionic synthetic detergents derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. For example, 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 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide; said base having a molecular weight of the order of 2,500 to 3,000 are satisfactory.

(4) The condensation product 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 alcoholethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(5) The ammonia, monoethanol and diethanol amides of fatty acids having an acyl moiety of from about 8 to about 18 carbon atoms. 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) Long chain tertiary amine oxides corresponding to the following general formula



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wherein R^1 is an alkyl radical of from about 8 to about 24 carbon atoms, R^2 and R^3 are each methyl, ethyl or hydroxyethyl radicals, R^4 is ethylene, and n equals 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; cetyldimethylamine oxide; bis-(2-hydroxyethyl) dodecylamine oxide; bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropyl amine oxide.

(7) Long chain tertiary phosphine oxides corresponding to the following general formula $RR'R''P \rightarrow O$ wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 24 carbon atoms in chain length 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 U.S. Patent 3,304,263 of Feb. 14, 1967 and include: dimethyldodecylphosphine oxide; diethyldodecylphosphine oxide; dimethyl-(2-hydroxydodecyl)phosphine oxide.

(8) 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; 3-hydroxy tridecyl methyl sulfoxide; 3-methoxy tridecyl methyl sulfoxide; 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

(d) Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are 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 may be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g. carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate which are especially preferred for their excellent cool water detergency characteristics. See, for example, Snoddy et al., Canadian Patent 708,148 issued Apr. 20, 1965.

PROCESS

The laundry composition of this invention is prepared by attaching the powdered enzyme to the granular carrier in the presence of water so as to achieve the desirable composition characteristics described above. The water employed in such attachment ranges from about 1% to about 25% by weight of the hydratable salt employed as or in the granular carrier. The preferred range is 5-15%. Water in these ranges is sufficient to permit efficient handling of the enzyme and carrier and to accomplish the enzyme attachment satisfactorily. An amount of water greater than that necessary for these purposes is preferably avoided so as to leave a maximum increment of hydratability in the partially-hydrated hydratable salt of the granular carrier.

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The water can be employed in the process of this invention to effect the desired enzyme attachment in any of the following methods, all of which use agitation:

(1) Water can be used to wet granular carrier followed by prompt application to the wetted carrier granules of the powdered enzyme;

(2) Water can be added to a dry mechanical mixture of the granular carrier and the powdered enzyme;

(3) The granular carrier, powdered enzyme and water can be added together at about the same time;

(4) Powdered enzyme can be slurried with water and the resulting slurry sprayed onto the granular carrier.

In methods (1), (2) and (3), water is added to the system uniformly, preferably with a fine spray and agitation of the particulate materials. Water can be sprayed while the carrier and enzyme are being agitated in a mixer such as a cement mixer, ribbon blender, rotating drum or pan agglomerator, or the water can be sprayed on the carrier and enzyme which are in the form of a falling curtain of the dry particulate components. The apparatus described in U.S. Patent 3,154,496, Roald, of Oct. 27, 1964 can be used. Greater enzyme attachment on a weight basis can be effected by methods (2) and (3) than by methods (1) and (4). The added water of methods (2) and (3) can contain more of the same enzyme powder or a different enzyme powder. When method (4) is employed, the enzyme slurry is applied to the granular carrier, preferably in a fine spray while the granular carrier is being agitated as for methods (1)-(3).

The amount of water used in the process of this invention, including methods (1)-(4), should be sufficient to effect the desired attachment, but without exceeding about 90%, preferably 50% of the total hydration capacity of the hydratable salt. This amount of water usually ranges from 1% to 25%, preferably 5% to 15%, by weight of the hydratable salt. The water for preparing a slurry of powdered enzyme should be sufficient to permit easy handling of the slurry, i.e., to make it pumpable and sprayable. Preferably just enough water is employed for this purpose. The exact amount of water for this purpose will vary somewhat with the type of enzyme and the type of powder vehicle which might be associated with the enzyme and preferably ranges from about 1 to about 3 parts of water per part of enzyme product (enzyme + powdered vehicle). More than about 3 parts water is usually unnecessary and can result in an undue amount of water in the hydratable salt; less than about 1 part water presents spraying problems, e.g. nozzle clogging and pumping difficulties.

The attachment techniques should be practiced at ordinary temperatures, i.e., at less than about 150° F., preferably at less than 100° F.

It was surprising that the enzyme powder attaches to the granular carrier so readily, attaches so firmly and remains stable during and after the attachment process, even though water is employed to perform the attachment.

UTILITY

The laundry composition and detergent of this invention are effective in cleaning applications in hard and soft water, especially in removing, or making more removable, soils, stains and other foreign materials from textiles and fabrics. For example, they effectively make removable or remove the most commonly found soil on garments: skin flakes or other keratin, and lipid mixtures of triglycerides, wax esters, hydrocarbons, free fatty acids, sterols and lipoproteins, e.g. blood, pus, gravy, egg yolk, paint, grease, oil and grass stains. If the enzyme employed has amolytic activity, the detergent compositions of this invention, including those of the examples, have special usefulness for dishwashing and cleaning pots and pans in addition to laundering soiled fabrics.

EXAMPLES

The proportions and percentages of enzyme components given in the examples do not refer to active enzymes

but to powdered enzyme products comprising active enzyme and its powdered vehicle. "Alcalase," for example, as described above, contains 6% of active enzyme.

In Examples I-V the enzyme slurry is sprayed onto the granular carrier in a cement mixer with spray nozzles located outside the mixer with the spray being directed inwardly.

In Examples I-V, enzyme activity can be determined by a casein method. According to this test method, a specific amount of casein, a phosphoprotein of milk, is dissolved in water and then a specific amount of the enzyme composition is added to the casein solution. This mixture is retained at a constant temperature for a standard length of time. The reaction between the enzymes and the casein is stopped with a strong acid, e.g., hydrochloric or sulfuric acid. The excess casein is precipitated and then filtered from the mixture. The excess acid is titrated with a strong base. The amount of base required to neutralize the acid is an indication of enzymatic activity. This method is more fully explained in Glick (Ed.), *The pH-Stat and Its Uses in Biochemistry, Methods of Biochemical Analysis*, volume 4, pages 171-211 (1957) and Dixon and Webb (Eds.), *Enzymes*, pages 23-24 (1958).

In the examples all listings of water in the several formulations refer to water in the form of water of hydration either in the granular carrier and/or the hydratable salts which are admixed with the granular carrier, e.g., spray dried synthetic detergent granules.

The composition and process of this invention are illustrated by the examples which follow. Examples are not to be regarded as limiting the invention. All amounts, percentages and ratios in the specifications and claims are by weight unless otherwise indicated.

Example I

Granular detergent compositions A, B and C are prepared and have the following formulations:

Components	Percent		
	A	B	C
Sodium C ₁₂ alkyl benzene sulfonate (derived from tetrapropylene).....	31.8	32.4	35.0
Sodium tripolyphosphate.....	30.7	22.7	24.5
Sodium silicate.....	6.1	6.2	6.7
Sodium sulfate.....	8.8	9.0	9.7
Tetrasodium pyrophosphate (Na ₄ P ₂ O ₇).....		6.8	
Alcalase (proteolytic enzyme).....	0.72	0.72	0.72
Water.....	8.7	8.8	9.5
Miscellaneous detergent additives.....	Balance to 100%		

A. An aqueous slurry containing 38.7% Alcalase and 61.3% water is sprayed onto sodium tripolyphosphate in anhydrous granular form having a particle size ranging from about 0.2 mm. to about 1 mm. The resulting granular carrier has attached thereto 8% proteolytic enzyme powder, 78% partially hydrated sodium tripolyphosphate and 14% water as water of hydration. The carrier with attached enzyme is then mechanically mixed with other detergent ingredients, in the form of spray-dried granules of approximately the same size as the granular sodium tripolyphosphate, to form Composition A.

B. An aqueous slurry containing 38.7% Alcalase and 61.3% water is sprayed onto tetrasodium pyrophosphate in anhydrous granular form having a particle size ranging from 0.2 mm. to 1 mm. The resulting granular carrier has attached thereto 10.4% proteolytic enzyme powder, and comprised 79.0% partially hydrated Na₄P₂O₇ and 16.4% water as water of hydration. The carrier with attached enzyme then is mechanically mixed with detergent ingredients, in the form of spray-dried granules of approximately the same size as the pyrophosphate granules, to form Composition B.

C. Composition C is prepared by dry-mixing the same amount of enzymes as used in compositions A and B with detergent ingredients in the form of spray-dried

granules. The powdered enzyme tends to segregate from the spray-dried granules.

In testing Compositions A, B and C for stability, A and B, overall, show superior stability, over conditions of time and humidity, relative to C. The powdered enzyme does not segregate significantly in Composition A and B.

Example II

The following granular detergent compositions A, B and C are prepared:

Components	Percent		
	A	B	C
Sodium C ₁₀₋₁₄ alkyl benzene sulfonate.....	18.9	17.2	22
Lauric monoethanol amide.....	2.1	1.9	2.4
Sodium tripolyphosphate.....	31.8	35.8	43.8
Sodium silicate.....	5.0	4.5	5.8
Sodium sulfate.....	12.9	12.1	15.4
Sodium perborate.....	20.0	20.0	
Alcalase (proteolytic enzyme).....	0.6	0.6	0.6
Water.....	5.3	6.4	6.8
Miscellaneous detergent additives.....	Balance to 100%		

Detergent composition A is prepared by dry-mixing the proteolytic enzyme powder with spray-dried detergent granules. Detergent compositions B and C employ a granular carrier having attached thereto the proteolytic enzyme powder. The carrier with attached enzyme is prepared by spraying an aqueous slurry containing 34% Alcalase powder onto anhydrous granular sodium tripolyphosphate of the type used in Example I. The carrier with enzyme contains 8.1% Alcalase attached to 76% partially-hydrated sodium tripolyphosphate granular carrier, the balance being water of hydration. The carrier with enzyme is mechanically mixed with other detergent ingredients, which are in the form of spray-dried granules of about the same particle size as the carrier, to form compositions B and C.

In testing Compositions A, B and C for stability, Compositions B and C demonstrate stability superior to Composition A. Moreover, segregation of enzyme powder is a problem in Composition A whereas no such problem is faced in Compositions B and C.

Example III

The following granular detergent compositions are prepared:

Components	Parts by weight			
	A	B	C	D
Sodium C ₁₂ alkyl benzene sulfonate (derived from tetrapropylene).....	23.8	23.8	12.9	12.9
Lauric monoethanol amide.....	2.5	2.5	1.4	1.4
Sodium tripolyphosphate.....	40.0	40.0	61.0	61.0
Sodium silicate.....	6.3	6.3	3.5	3.5
Sodium sulfate.....	16.6	16.6	9.1	9.1
Proteolytic enzyme.....	5.0 (a)	5.0 (b)	1.58 (a)	1.9 (b)
Water.....	7.4	7.4	7.7	7.7

In compositions A and B, the powdered enzymes (a) and (b) are incorporated into the granular detergent compositions by dry-mixing. For compositions C and D, the powdered enzymes, (a) and (b) are prepared by spraying aqueous slurries containing 35% enzymes and 65% water onto anhydrous granular sodium tripolyphosphate of the type of Example I. The granular carriers with attached enzyme powder obtained from this operation contained about 4.5% enzyme, 87% partially hydrated sodium tripolyphosphate and 8.5% water of hydration and are then mixed into the other granular detergent ingredients which are in spray-dried granular form to prepare Compositions C and D. Proteolytic enzyme (a), (Rapidase P-2000 manufactured by Rapidase, Seclin, France), and (b), (Protease AP manufactured by Schweizerische Ferment, A.G., Basel, Switzerland), contain approximately one-tenth the amount of proteolytic enzyme contained in Alcalase.

Compositions C and D have stability and nonsegrega-

tion characteristics markedly superior to Compositions A and B.

Example IV

The following granular detergent compositions A, B, C and D are prepared:

Components	Percent			
	A	B	C	D
Sodium C ₁₀₋₁₄ alkyl benzene sulfonate	22.1	22.7	22.7	23.7
Lauric monoethanol amide	2.4	2.5	2.5	2.6
Sodium tripolyphosphate	42.3	38.0	38.5	40.0
Sodium silicate	5.9	6.0	6.0	6.3
Tetrasodium pyrophosphate		3.3		
Disodium pyrophosphate (Na ₂ H ₂ P ₂ O ₇)			2.6	
Sodium sulfate	15.4	14.7	16.0	16.6
Proteolytic enzyme (Alcalase)	0.5	0.6	0.5	0.6
Water	6.8	7.1	7.1	7.4
Miscellaneous detergent additives		Balance to 100%		

For detergent composition A, the enzyme is prepared by spraying an aqueous slurry containing 40% Alcalase and 60% water onto anhydrous granular sodium tripolyphosphate of the type of Example I (pH of 1% solution 9.7). The granular carrier with attached powdered enzyme powder so obtained contain about 8% enzyme, 80% partially hydrated sodium tripolyphosphate and 12% water of hydration. The carrier is mixed with other detergent components which are in the form of spray-dried detergent granules of approximately the same particle size as the carrier. Composition B is similarly prepared but using anhydrous granular Na₄P₂O₇ of similar particle size (pH at 1% solution:10:1).

Composition C is prepared in the same manner as A or B; the enzyme is sprayed onto anhydrous granular Na₂H₂P₂O₇ (pH of 1% solution: 4.2) and vapor pressure of less than 13.15 mm. of Hg at 20° C. and one atmosphere.

In composition D, the enzyme powder is dry-mixed into the detergent composition which is in the form of spray-dried granules.

The composition of this invention (A, B and C) are superior in stability to the dry-mixed composition (D) and do not have the segregation disadvantage of the dry-mixed composition.

Example V

In this example, an enzyme (Alcalase) is mixed with water and sprayed onto granular, anhydrous, sodium tripolyphosphate.

More specifically, 258 grams of Alcalase are added to a glass beaker containing 516 grams of water at room temperature, 70° F. This mixture is agitated by hand with a spatula until a fluid, homogeneous dispersion is obtained. This dispersion has a viscosity slightly greater than that of water and a pH of about 7.0.

Five kilograms of granular, anhydrous, sodium tripolyphosphate having a particle size distribution ranging from about 100% of the granules through a Tyler Standard 12 mesh screen to about 100% of the granules on a Tyler Standard 100 mesh screen and a density of 0.7 gms./cc. are placed in a baffled cement mixer. The mixer is then started.

An aspirator unit operated by air pressure is placed in the beaker containing the dispersion of enzyme in water. The dispersion of enzyme in water is evacuated from the beaker and sprayed onto the sodium tripolyphosphate granules. The water is bound to the sodium tripolyphosphate as water of hydration and the powdered enzyme is attached to the partially hydrated tripolyphosphate granules. This composition contains about 4.5% attached Alcalase powder and about 9% water of hydration.

361 grams of this granular sodium tripolyphosphate carrier with attached enzyme are mechanically mixed with 7.5 kilograms of a spray-dried granular detergent of ap-

proximately the same particle size as the tripolyphosphate carrier containing in parts by weight:

Percent by weight	
A mixture of 55% sodium tallow alkyl sulfate and 45% sodium linear alkyl benzene sulfonate wherein the alkyl chain distribution 16% C ₁₁ , 27% C ₁₂ , 35% C ₁₃ and 22% C ₁₄	17.5
Sodium tripolyphosphate	50.0
Sodium silicate having an SiO ₂ :NaO ratio of 1.8:1	6.0
Coconut fatty acid ammonia amide	2.5
Sodium sulfate	14.0
Water	10.0

The resulting detergent composition has a density of about 0.7 gms./cc., and its recommended usage in ordinary washing machines is one-half cup. It exhibits superior stability and laundering characteristics and no segregation problems relative to the powdered enzyme.

Example VI

Detergent granules were prepared from the following components:

Parts by weight	
Anionic paste	35.64
Sodium tripolyphosphate	69.0
Water	27.80
Sodium sulfate	4.48

The anionic paste contained, in parts by weight:

Sodium tallow alkyl sulfate	5.06
Sodium linear alkyl benzene sulfonate (see Example V)	4.14
Sodium sulfate	6.16
Water	20.28

Total 35.64

The components described above were slurried and then spray-dried to a moisture level of 2.18% moisture (water of hydration). The density of the resulting granular detergent composition was about 0.40 gms./cc. The particle size distribution ranged from a maximum of about 99% through a Tyler Standard 14 mesh screen to about 100% retained on a Tyler Standard 100 mesh screen.

A slurry containing 1.5 parts of water per part of Alcalase powder was prepared and 10 parts of this slurry were sprayed onto 92 parts of the detergent granules. The detergent granules were formed into a falling curtain in a pan agglomerator and the water-Alcalase mixture was sprayed uniformly on the falling particles. The water was bound as water of hydration and the Alcalase was attached to the surfaces of the partially hydrated granules. The hydrate vapor pressure of the finished granules corresponded to a relative humidity of less than 70% at one atmosphere pressure and 20° C. The granular carrier with attached powdered enzyme contained, in parts by weight:

Granular carrier (partially hydrated)	92
Alcalase	4
Water of hydration	6

When Monsanto DA-10 (40% active protease) replaces the Alcalase on an equal weight basis in this example similar results are obtained except that greater enzyme activity is obtained.

These granules can be dyed a bright color to give the detergent composition a distinctive appearance, especially when admixed with the granular detergent composition of Example VII.

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Example VII

A granular detergent composition is prepared from the following components:

	Parts
Anionic paste of Example VI-----	65.26
Sodium tripolyphosphate -----	45.93
Sodium silicate solution (43% solids=57% water) -----	13.79
Coconut fatty acid monoethanol amide-----	1.35
Sodium sulfate -----	1.00

These components are slurried and then spray-dried to a moisture level of 10.2%. The particle size distribution ranges from about 100% through a Tyler Standard 12 mesh screen to about 100% on a Tyler Standard 100 mesh screen and the density is about 0.4 gms./cc.

5 parts of the granular carrier with attached enzyme produced in Example VI are mixed with 95 parts of the detergent granules of Example VII. This mixture is suitable for use as a heavy-duty laundry detergent. It is particularly effective for removing stains of all types on both white and colored washable fabrics. The enzyme powder does not segregate from the rest of the granular detergent composition.

In the following table, the mixture of Example VII (VII-1, 2 and 3) is compared to a product of about the same formulation but wherein Alcalase powder is simply dry mixed with the detergent granules of Example VII to form product #4. The products were packaged in cardboard containers for this storage test.

Days:	Product			
	VII-1	VII-2	VII-3	4
	Test Conditions			
	70° F. Ambient Humidity	120° F. Ambient Humidity	90° F./80% Relative Humidity	90° F./80% Relative Humidity
0	-----	0.295	0.295	0.295
4	-----	-----	-----	0.21
7	-----	-----	-----	0.17
9	-----	0.30	0.33	0.27
12	-----	-----	-----	0.14
14	-----	0.32	0.32	0.25
17	-----	-----	-----	0.27
20	-----	-----	-----	0.037
21	-----	-----	0.26	-----
28	-----	-----	0.23	-----
29	-----	0.33	-----	-----
34	-----	-----	0.20	-----
35	-----	0.27	-----	-----

In a 20 days period, the dry-mixed detergent composition, Product #4, lost nearly 85% of its enzymatic activity. The detergent composition of this invention, VII-1, 2 and 3, showed essentially no less in enzymatic activity over protracted time periods.

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

Example VIII

In this example a ribbon blender having overhead water sprays was employed. To the blender were added 100 kilograms of enzyme powder (Alcalase) and 340 kilograms of granular anhydrous sodium tripolyphosphate having a particle size ranging from 0.2 mm. to 1 mm. and a bulk density ranging from .44 to .51 grams per cc. While the enzyme powder and the granular sodium tripolyphosphate were being intimately mixed, 60 kilograms of water were added through the overhead sprays over a mixing time of 15 minutes. The resulting 500 kilograms of granular sodium tripolyphosphate carrier with the powdered enzyme attached contained 12% water as water of hydration, 5 parts of the carrier and enzyme

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can be mixed with 95 parts of the detergent granules of Example VI to form a detergent composition.

Example IX

An enzyme-water slurry of Example VI is prepared and sprayed onto sodium tetraborate granules employing the spraying technique used in Example VI. The borate granules have a density of 0.5 gm./cc., a particle size ranging from 1.4 to 0.14 mm. and a moisture content of 2%. The resulting granular carrier with attached enzyme comprised 92 parts partially hydrated sodium tetraborate, 4 parts Alcalase and 6 parts water of hydration.

5 parts of the carrier and enzyme of this example are mixed with 95 parts of the detergent granules of Example VI. The resulting granular detergent composition is suitable for use as a heavy-duty laundry detergent. The granular carriers with attached enzyme do not segregate from detergent granules in the packaged product. The stability of the attached enzyme is enhanced.

Example X

In this example, results substantially similar to those in Examples VIII and IX are obtained when other enzyme powders are substituted, either wholly or in part, for Alcalase to provide partially hydrated tripolyphosphate and borate granular carriers with attached enzymes which are useful laundry compositions having improved stability and segregation characteristics. The commercial enzyme powders that can be substituted for Alcalase to obtain the desirable advantages of this invention are Maxatase, Protease B-4000, Protease AP, CRD Protease, Viokase, Pronase-P, Pronase-AS, Pronase-AF, Rapidase P-2000, Takamine, Bromelain 1:10, HT Proteolytic Enzyme 200, Enzyme L-W, Rhozyme P-11 Concentrate, Pectinal, Lipase B, Rhozym PF, Rhozyme J-25, Amprozyme 200. Other classes of enzymes which can be substituted for Alcalase are pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, ficin, subtilisin, BPN', papain, bromelin, carboxylase, amino peptidase, aspergillopeptidase A, aspergillopeptidase B, gastric lipase, pancreatic lipase, plant lipases, phosphilapases, cholinesterases, phosphotases, maltase, saccharase, amylase, cellulase, pectinase, lysozyme, α -glycosidase, β -glycosidase, ribonuclease and desoxy ribonuclease.

All of the enzymes of this example have the desired enzymatic activity and are obtained and stored in a dry, powdered form. The enzymes have particle size diameters ranging from about 1 mm. to 1 micron, generally from 0.1 mm. to 0.01 mm. The enzymes have an active enzyme content in the range of about 2% to about 80%.

Example XI

When the following hydratable salts, or mixtures thereof are substituted, either wholly or in part, for the hydratable salts of Example X, results similar to those of Example X are obtained. The salts are employed in an anhydrous or slightly hydrated form at the beginning of the attachment process. Sufficient water is employed to effect the desired attachment and to partially hydrate the hydratable salt up to 30 to 50% of its total hydration capacity. The hydratable salts are: sodium sulfate, ammonium pyrophosphate, sodium hexametaphosphate, trisodium ethylenediaminetetraacetate, tripotassium N-(2-hydroxyethyl)-ethylenediaminetriacetate, trisodium nitrilotriacetate, tetrasodium ethane-1-hydroxy-1,1-diphosphonates, trilithium methylene diphosphonate, trisodium ethylene diphosphonate, pentasodium ethane-1,1,2-triphosphonate, disodium ethane-2-carboxy-1,1-di-phosphonate, dipotassium carbonyl-diphosphonate, tetrasodium ethane-2-hydroxy-1,1,2-triphosphonate, pentasodium propane-1,1,3,3-tetraphosphonate and tri(triethanol ammonium) isopropylidene diphosphonate. The hydratable salts have a particle size distribution such that not more than about 30% of the granules are retained on a Tyler Standard 14 mesh screen and no more than 7% of the granules pass through a Tyler Standard 100 mesh screen.

Generally, the particle size distribution is such that about 100% of the granules pass through a Tyler Standard 12 mesh screen and about 100% of the granules are retained on a Tyler Standard 100 mesh screen. Preferably these hydratable builder salts are employed in a form in which average bulk densities range from 0.2 gms./cc. to 0.8 gms./cc, e.g. 0.5 gms./cc.

Example XII

When in Example I, any of the following detergents are substituted for the sodium alkyl benzene sulfonate detergent substantially similar results are obtained: sodium coconut soap, sodium linear alkyl benzene sulfonate having a chain length distribution of 10% C₁₀, 30% C₁₁, 35% C₁₂, 16.5% C₁₃, 8% C₁₄ and 0.5 C₁₅, sodium tallow alkyl sulfate; the condensation product of one mole of coconut alcohol with 5 moles of ethylene oxide; the condensation product of one mole of octyl phenol with 20 moles of ethylene oxide; the condensation product of one mole of coconut alcohol with 20 moles of ethylene oxide; dimethylhydroxydodecylamine oxide; cetyldimethylphosphine oxide; sodium-3-dodecylaminopropionate; and 3-(N,N-dimethyl - N - decylammonio)-2-hydroxypropane-1-sulfonate.

The foregoing description of the invention has been presented describing certain preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of this invention.

What is claimed is:

1. A granular laundry composition consisting essentially of a powdered enzyme composition attached to a water-soluble granular carrier which consists essentially of 20% to 100% of a partially hydrated hydratable salt which has a pH in aqueous solution in the range of 4 to 12 and a vapor pressure not greater than about 13.15 mm. of Hg when measured at atmospheric pressure at 20° C., which is hydrated not in excess of 90% of its hydration capacity, and which is selected from the group consisting of alkali metal, alkaline earth metal and ammonium detergency builder salts having a pH of 4 to 12, fatty acid soaps of 10 to 18 carbon atoms, CaCl₂ and mixtures of said salts, said powdered enzyme composition being from about .001% to about 40% by weight of said laundry composition, consisting essentially of 2% to 80% active enzyme and 98% to 20% inert powdered vehicle and being attached to said carrier as result of hydration of said carrier salt, wherein said vehicle consists essentially of a material selected from the group consisting of calcium salts, sodium sulfate, sodium chloride, clays and starch and wherein the said carrier has a particle size in the range of about 0.075 mm. to about 3.33 mm.

2. The laundry composition of claim 1 wherein the carrier has a particle size in the range of 0.2 mm. to 2 mm., the hydratable salt is a hydratable builder salt which has a pH in aqueous solution in the range of 8 to 11 and the inert powdered vehicle consists essentially of a calcium salt.

3. The laundry composition of claim 2 wherein the active enzyme is a hydrolase and the hydratable salt is not more than about 50% hydrated, based on its total hydration capacity, and the hydratable builder salt is selected from the group consisting of sodium tripolyphosphate, sodium pyrophosphate and sodium tetraborate.

4. The laundry composition of claim 3 wherein the hydrolase is selected from the group consisting of proteases, esterases, carbohydrases and nucleases and the hydratable builder salt is sodium tripolyphosphate.

5. The laundry composition of claim 4 wherein the active enzyme is a serine protease and the powdered enzyme composition is in an amount ranging from about .001% to about 20% of the total weight of the said laundry composition.

6. A granular detergent composition consisting essentially of about 0.2% to about 30% of the granular laundry composition of claim 2 mechanically admixed with from about 99.8% to about 70% of enzyme-free detergent granules which consist essentially of a water-soluble organic detergent and a water-soluble detergency builder salt, wherein the ratio of detergent to builder salt is in the range of 4:1 to 1:20.

7. A process for preparing the laundry composition of claim 3 which comprises the steps of (a) wetting said carrier, wherein the said hydratable salt is initially in an anhydrous or partially hydrated state, with an amount of water which is from 1% to 25% of the hydratable salt and insufficient to hydrate the said hydratable salt more than about 50% of its hydration capacity, (b), promptly thereafter said wetting, applying said powdered enzyme composition to said wetted carrier, with agitation, to effect the attachment of said enzyme composition to said carrier and to effect a further partial hydration of said salt.

8. A granular detergent composition consisting essentially of about 0.2% to about 30% of the granular laundry composition of claim 3 mechanically admixed with from about 99.8% to about 70% of enzyme-free detergent granules which consist essentially of a water-soluble organic detergent and a water-soluble detergency builder salt wherein the ratio of detergent to builder salt is in the range of 4:1 to 1:20.

9. A granular detergent composition consisting essentially of about 0.2% to about 30% of the granular laundry composition of claim 4 mechanically admixed with from about 99.8% to about 70% of enzyme-free detergent granules which consist essentially of an anionic organic synthetic detergent and sodium tripolyphosphate builder salt wherein the ratio of detergent to builder salt is in the range of 4:1 to 1:20.

10. A process for preparing the laundry composition of claim 3 comprising the steps of (a) agitating said carrier wherein the hydratable builder salt is in an anhydrous or partially hydrated state and (b) subjecting said agitated carrier to a fine spray of a mixture of said enzyme composition and water to effect a partial hydration of said hydratable salt, thereby attaching said powdered enzyme composition to said carrier, the amount of water being from 1% to 25% of the hydratable builder salt and insufficient to hydrate said salt to more than 50% of its hydration capacity.

11. A process for preparing the laundry composition of claim 5 comprising the steps of (a) mixing said powdered enzyme composition in an initially dry state with said carrier wherein the hydratable builder salt is in an anhydrous or partially hydrated state and (b) subjecting the resulting mixture to a fine spray of water and simultaneous agitation to effect a partial hydration of said hydratable salt, thereby attaching said powdered enzyme composition to said carrier, the amount of water being from 1% to 25% of the hydratable builder salt and insufficient to hydrate said salt to more than 50% of its hydration capacity.

12. A process for preparing the laundry composition of claim 5 comprising the steps of (a) agitating said carrier wherein the hydratable builder salt is in an anhydrous or partially hydrated state, and (b) subjecting said agitated carrier to a fine spray of a mixture of said enzyme composition and water to effect a partial hydration of said hydratable builder salt, thereby attaching said powdered enzyme composition to said carrier, the amount of water being from 1% to 25% of the hydratable builder salt, insufficient to hydrate said salt to more than 50% of its hydration capacity, and ranging from 1 to 3 parts water per part of said powdered enzyme composition.

13. A process for preparing the laundry composition of claim 1 comprising the steps of (a) mixing said powdered enzyme composition in an initially dry state with said carrier wherein the hydratable salt is in an anhydrous or

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partially hydrated state and (b) subjecting the resulting mixture to a fine spray of water and simultaneous agitation to effect a partial hydration of said hydratable salt, thereby attaching said powdered enzyme composition to said carrier, the amount of water being in an amount from 1% to 25% of the hydratable salt and insufficient to hydrate said salt to more than 90% of its hydration capacity.

14. A process for preparing the laundry composition of claim 1 comprising the steps of (a) agitating said carrier wherein the hydratable salt is in an anhydrous or partially hydrated state and (b) subjecting said agitated carrier to a fine spray of a mixture of said enzyme composition and water to effect a partial hydration of said hydratable salt, thereby attaching said powdered enzyme composition to said carrier, the amount of water being from 1% to 25% of the hydratable salt and insufficient to hydrate said salt to more than 90% of its hydration capacity.

15. A process for preparing the laundry composition of claim 2 comprising the steps of (a) mixing said powdered enzyme composition in an initially dry state with said carrier wherein the hydratable builder salt is in an anhydrous or partially hydrated state, and (b) subjecting the resulting mixture to a fine spray of water and simultaneous agitation to effect a partial hydration of said hydratable builder salt, thereby attaching said powdered enzyme composition to the said carrier, the amount of water being in an amount from 1% to 25% of the hydratable builder salt and insufficient to hydrate said salt to more than 90% of its hydration capacity.

16. A process for preparing the laundry composition of claim 2 comprising the steps of (a) agitating said carrier, wherein the hydratable builder salt is in an anhydrous or partially hydrated state, and (b) subjecting said agitated carrier to a fine spray of a mixture of said enzyme composition and water to effect a partial hydra-

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tion of said hydratable builder salt, thereby attaching said powdered enzyme composition to said carrier, the amount of water being from 1% to 25% of the hydratable builder salt and insufficient to hydrate said salt to more than 90% of its hydration capacity.

17. A process for preparing the laundry composition of claim 1 which comprises the steps of (a) wetting said carrier, wherein the said hydratable salt is initially in an anhydrous or partially hydrated state, with an amount of water which is from 1% to 25% of the hydratable salt and insufficient to hydrate the said hydratable salt more than about 50% of its hydration capacity, (b), promptly thereafter said wetting, applying said powdered enzyme composition to said wetted carrier, with agitation, to effect the attachment of said enzyme composition to said carrier and to effect a further partial hydration of said salt.

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195—63, 68; 252—89, 132, 137; 424—94

Dedication

3,451,935.—*Arnvid S. Roald*, Wezembeek-Oppem Brabant, and *Nicolaas T. de Oude*, Brussels, Belgium. GRANULAR ENZYME-CONTAINING LAUNDRY COMPOSITION. Patent dated June 24, 1969. Dedication filed Dec. 29, 1969, by the assignee, *The Procter & Gamble Company*.

Hereby dedicates the entire remaining term of said patent to the Public.
[*Official Gazette July 21, 1970.*]