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ENZYME-CONTAINING DETERGENT COMPOSITIONS AND A PROCESS FOR CONGLUTINATION OF ENZYMES AND DETERGENT COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Granular, enzyme-containing detergent compositions wherein the stability of the enzymes is enhanced and a process for making said enzyme-containing detergent compositions by rendering the surfaces of detergent granules glutinous with a low melting, ordinarily solid nonionic surface active agent and conglutinating, with the glutinous detergent granules, powdered enzymes which are active in the pH range of from about 4 to about 12 and the temperature range of from about 50° F. to about 185° F.

CROSS REFERENCES

This application is a continuation-in-part of applicant's copending applications Ser. No. 544,846, filed Apr. 25, 1966, now abandoned, and Ser. No. 620,608, filed Mar. 6, 1967, now abandoned.

FIELD OF INVENTION

This invention relates to enzyme-containing detergent compositions and to a process for conglutinating enzymes and detergent compositions.

PRIOR ART

Enzymes have been used as cleaning aids for many years. As early as 1915, Rohm had found that fabrics could be cleaned more easily and at lower temperatures when pretreated with fat and protein digesting enzymes. See Rohm, German Pat. 283,923 (May 15, 1915). Later, in 1932, enzymes were utilized in a soap composition having greatly improved cleansing action. See Frelinghuysen, U.S. Pat. 1,882,279 (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 nonuniform 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 conditions 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.

OBJECTS

Accordingly, an object of this invention is to provide a granular detergent composition that contains enzymes. Another, more specific, object of this invention is to provide an enzyme-containing detergent composition wherein the enzymes remain uniformly distributed throughout the product and the stability of the enzymes in the detergent composition is enhanced. Another object of this invention is to provide a process for incorporating enzymes into a detergent composition which minimizes the contact of the enzymes with materials which are deleterious to the enzyme. Another object is to provide a preferred mild enzyme-containing composition.

Further objects will become apparent from the detailed description given hereinafter. All parts, percentages and ratios set forth herein are by weight unless otherwise indicated.

SUMMARY OF INVENTION

Enzyme powders are conglutinated with base granules having desired size characteristics by employing a water-soluble nonionic surface active agent as the conglutinating agent. Such conglutination improves the stability characteristics of the enzyme powder and reduces its segregation tendencies. In another aspect of this invention, mixtures of enzymes, and inorganic per compounds, conglutinated or not have unexpected mildness properties. Base granules are detergent granules, as described hereinafter, to which enzymes are attached and which have not yet been conglutinated with enzymes. When enzymes are attached to the base carrier granules, the resultant granules, comprising base granules and attached enzymes are referred to as finished granules.

DETAILED DESCRIPTION OF INVENTION

Summary of process and product

The process of this invention comprises the steps of:

(1) Rendering the surfaces of base granules having a particle size distribution such that about 100% of the granules pass through a Tyler Standard 6 mesh screen and about 100% of the granules are retained on a Tyler Standard 200 mesh screen (i.e., ranging in particle size from about .075 mm. to about 3.3 mm.) and having an average bulk density of from about 0.2 gm./cc. to about 0.8 gm./cc., glutinous with from about 3% to about 90%, preferably 5% to 15%, by weight of said base granules of a low melting, ordinarily solid, water-soluble nonionic surface active agent which liquefies between the temperatures of from about 110° F. to about 200° F. and which is solid at temperatures below 110° F.; and

(2) Conglutinating with said glutinous surfaces of said base granules to form finished granules from about 0.001% to about 40% by weight of the finished granules of enzymes, conglutinated in a powdered active enzyme or enzyme composition form; when enzyme compositions are employed the amount ranges from about 0.001% to about 60% by weight of the finished granules, and said active enzymes being active in the pH range of from about 4 to about 12 and the temperature range of from about 50° F. to about 185° F.

The product of this invention is that which results from this process. The finished granules comprise base granules having a partial or complete nonionic coating thereon. The nonionic at least partially encapsulates the powdered enzymes and acts as the conglutinating agent for the base granules and the powdered enzymes.

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. 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.

Enzymes suitable for use in this invention are those active in a pH range of from about 4 to about 12 and, preferably, are active 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 Biochemistry, (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 large 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 addititon or removal of water and degrade soil, especially of a protein type.

(A) Hydrolyzing enzymes (hydrolases).
  (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 analagous 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 (demolases) 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 oxidoreductases.

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 breakdown 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 are 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 carbohydate 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 desoxyribonuclease.

All of the enzymes described herein are utilized in this invention in a dry, powdered form. It is desirable that the enzymes be used in a dry form as degradation of the enzymes is minimized. The powdered form of enzymes is most easily handled in the conglutination process hereinafter described and is, therefore, preferred.

The enzymes per se have molecular diameters of from about 30 angstroms to several thousand angstroms. However, the particle diameters of the enzyme powder as utilized herein are normally much larger due to agglomeration of individual enzymes molecules or addition of inert vehicles such as starch, organic clays, sodium of 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 combination of enzyme and inert vehicle usually comprises from about 2% to about 80% active 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, most generally from 1 mm. to 0.01 mm. The enzyme powders of the examples have particle size distributions 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 or sodium chloride 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 finished granules have 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. Some of these commercial products contain, in addition to the proteases, lipases, carbohydrases, esterases and nucleases. Other commercial products contain only lipases, carbohydrases, esterases and nucleases.

Specific examples of commercial enzyme products and the manufacturer thereof include: Alcalase, Novo Industri, Copenhagen, Denmark; Maxatase, Koninklijke Nederlandsche Gist-En Spiritusfabriek N.V., Delft, Netherlands; Protease B–4000 and Protease AP, Schweizerische Ferment A.G., Basel, Switzerland; CRD-Protease, Monsanto Company, St. Louis, Mo.; Viokase, VioBin Corporation, Monticello, Ill.; Pronase-P, Pronase-AS and Pronase-AF all of which are manufactured by Kaken Chemical Company, Japan, Rapidase P–2000, Rapidase, Seclin, France; proteolytic enzyme products (particle sizes ranging from about 100% through a Tyler Standard 16 mesh screen to about 100% on a Tyler Standard 150 mesh screen) manufactured by Clinton Corn Products, Division of Standard Brands, New York, N.Y.; Takamine, Bromelain 1:10, HT proteolytic enzyme 200, Enzyme L–W (derived from fungi rather than bacteria), Miles Chemical Company, Elkhart, Ind.; Rhozyme P–11 concentrate, Pectinol, Lipase B, Rhozyme PF, Rhozyme J–25, Rhom and Haas, Philadelphia, Pa., Rhozyme PF and J–25 have salt and corn starch vehicles and are proteases having diastase activity; Amprozyme 200, Jacques Wolf & Company, a subsidiary of Nopco Chemical Company, Newark, N.J.

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, manufactured by Novo Industri A/S, Copenhagen, Denmark, and sold under the trade name of Alcalase. Alcalase is described, in a trade bulletin bearing that name which was published by Novo Industri A/S, as a proteolytic enzyme preparation manufactured by submerged fermentation of a special strain of *Bacillus subtilis*. The primary enzyme component of Alcalase is substilisin. In addition to proteolytic activity, Alcalase exhibits other forms of desirable enzymatic activity. Alcalase is a fine grayish free-flowing 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 150 mesh Tyler screen. The remainder of the powder is comprised primarily of sodium sulfate, calcium sulfate and various inert organic vehicle materials. Alcalase has unusually 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 synthetic detergent compositions of this invention. Sequestrants such as EDTA can improve the stability of Alcalase.

The particular enzyme chosen for use in the products and process of this invention depends on the conditions of final utility, including the pH of the materials incorporated into the base granules, 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.

In the product and process of this invention, large variations in the amounts of active enzymes or enzyme compositions in the finished granules, i.e., those granules having enzymes attached thereto, are contemplated. For example, if finished granules with a high enzyme concentration are desired, as much as 40% by weight of the finished granules can be comprised of active enzymes or up to 60% by weight of the finished granules can be comprised of enzyme compositions (enzyme compositions refer to the combination of active enzymes and inert vehicle hereinbefore described). If finished granules having a low enzyme concentration are desired, the amount of active enzymes or enzyme compositions on the finished granules can be as low as 0.001% by weight of the finished granules. Accordingly, the finished granules of this invention can contain from about 0.001% to about 40% active enzymes by weight of the finished detergent granules or from 0.001% to about 60% enzyme compositions by weight of the finished detergent granules.

Finished detergent granules can be employed as such as a granular soaking or detergent composition or can be admixed with enzyme-free detergent granules of conventional types to form a soaking or detergent composition. Such admixtures are referred to herein as final detergent compositions.

In a preferred embodiment of this invention, the amount of active enzyme in a final detergent composition is from about 0.005% to about 4.0% by weight of the composition. When the preferred enzyme, Alcalase, is so utilized, the final detergent composition preferably contains from about 0.006% to about 0.12% active enzyme by weight. These figures correspond to a range of from about 0.1% to about 2.0% by weight of the final detergent composition of Alcalase.

Although the enzymes hereinbefore described perform well in alkaline solutions, acid solutions or solutions containing ionic organic detergents, the enzymes should be protected from such substances and from free water during storage. An ordinarily solid nonionic surface active agent, as hereinafter defined, performs this protective function. The nonionic is liquefied and then sprayed onto, or otherwise contacted with, the base granules. (The base granules are defined hereinafter.) As the nonionic cools, it becomes sticky or glutinous. Enzymes are then conglutinated with the glutinous surfaces of the base granules. After conglutination, a spray application of liquefied nonionic can be utilized to totally encapsulate the enzymes if desired.

Nonionic surface active agents

Ordinarily solid nonionic surface active agents which melt or liquefy between the temperature ofs about 110° F. and 200° F. and preferably between 120° F. and 150° F., and which dissolve or otherwise release the enzymes in aqueous solutions at ordinary washing temperatures, e.g., 120° F., can be utilized in the process of this invention for rendering the surfaces of the base granules glutinous or sticky. The temperature at which these particular nonionic surface active agents become tacky and glutinous is low enough to prevent degradation of the enzymes used in this process yet high enough to prevent caking of the detergent composition under ordinary storage conditions. While ionic surface active agents tend to degrade enzymes, these nonionics do not.

From about 3% to about 90% by weight of the base granules of the nonionic should be utilized in rendering the surfaces of the base granules glutinous. It is preferred that from about 5% to about 15% by weight of the base granules of nonionic be utilized to render the surfaces of the base granules glutinous in order to prevent segregation problems in the finished granules and any final detergent composition in which they are employed. It is further preferred that from about 0.05% to about 15% of nonionic by weight of a final detergent composition be utilized herein. When this invention is practiced within these preferred ranges, segregation of enzyme powder in the finished granules or in a final detergent composition is minimized and sudsing properties thereof are optimized.

Specific examples of suitable nonionic surface active agents for use in the process of this invention are:

(1) The condensation products of one mole of a saturated or unsaturated, straight or branched chain carboxylic acid having from about 10 to about 18 carbon atoms with from about 20 to about 50 moles of ethylene oxide, which liquefy between the temperatures of about 110° F. and about 200° F. and are solid at temperatures below about 110° F. The acid moiety can consist of mixtures of acids in the above delineated carbon atom range or it can consist of an acid having a specific number of carbon atoms within this range. The condensation product of one mole of coconut fatty acid having the approximate carbon chain length distribution of 2% C_{10}, 66% C_{12}, 23% C_{14} and 9% C_{16} with 35 moles of ethylene oxide is a specific example of a nonionic containing a mixture of different chain length fatty acid moieties. Other specific examples of nonionics of this type are: the condensation products of one mole of palmitic acid with 40 moles of ethylene oxide; the condensation product of one mole of myristic acid with 35 moles of ethylene oxide; the condensation product of one mole of oleic acid with 45 moles of ethylene oxide; and the condensation product of one mole of stearic acid with 30 moles of ethylene oxide.

(2) The condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohol having from about 10 to about 24 carbon atoms with from about 10 to about 50 moles of ethylene oxide, which liquefy between the temperatures of about 110° F. and 200° F. and are solid at temperatures below about 110° F. The alcohol moiety can consist of mixtures of alcohols in the above-delineated carbon atom range or it can consist of an alcohol having a specific number of carbon atoms within this range. The condensation product of one mole of coconut alcohol having the approximate chain length distribution of 2% C_{10}, 66% C_{12}, 23% C_{14} and 9% C_{16} with 45 moles of ethylene oxide ($CNAE_{45}$) is a specific and highly preferred example of a nonionic containing a mixture of different chain length alcohol moieties. Other specific examples of nonionics of this type are the condensation products of one mole of tallow alcohol with 20 moles of ethylene oxide; the condensation products of one mole of lauryl alcohol with 35 moles of ethylene oxide; the condensation products of one mole of myristyl alcohol with 30 moles of ethylene oxide; and the condensation products of one mole of oleyl alcohol with 40 moles of ethylene oxide.

(3) Two specific examples of nonionic surface active agents suitable for use in this invention and not specifically classified herein are polyoxyethylene glyceride esters having a hydrophile-lipophile balance (HLB) of 18.1 and polyoxyethylene lanolin derivatives having an HLB of 17:0. Both nonionics are manufactured by Atlas Chemical Industries, Inc.; the trade name of the former is G–1300 and the trade name of the latter is G–1795. The HLB number is an indication of the percentage weight of the hydrophilic portion of the nonionic molecule divided by 5.

(4) Certain amides which have a melting point between about 110° F. and 200° F. and which release the enzymes under the conditions of use as hereinbefore specified, are also suitable for use in this invention. Specific examples are propyl amide, N-methyl amides having an acyl chain length of from about 10 to about 15 carbon atoms, pentyl anilide and anilides having a carbon chain length of from about 7 to about 12 carbon atoms, oleamide, amides of ricinoleic acid, N-isobutyl amides of pelargonic acid, capric acid, undecanoic acid and lauric acid, N-(2-hydroxyethyl) amides having carbon chain lengths of from about 6 to about 10 carbon atoms, N-cyclopentyllauramide and N-cyclopentylstearamide.

(5) The polyethylene glycols having a molecular weight of from about 1400 to about 30,000. For example, Dow Chemical Company manufactures these nonionics in molecular weights of 20,000, 9500, 7500, 4500, 3400 and 1450. All of these nonionics are waxlike, solids which melt between 110° F. and 200° F.

(6) The condensation products of one mole of alkyl phenol wherein the alkyl chain contains from about 8 to about 18 carbon atoms with from about 25 to about 50 moles of ethylene oxide. Specific examples of these nonionics are the condensation products of one mole of decyl phenol with 40 moles of ethylene oxide; the condensation products of one mole of dodecyl phenol with 35 moles of ethylene oxide; the condensation products of one mole of tetradecyl phenol with 35 moles of ethylene oxide; the condensation products of one mole of hexadecyl phenol with 30 moles of ethylene oxide.

(7) Fatty acids containing from about 12 to about 30 carbon atoms which melt between 110° F. and 200° F. Specific examples of these nonionics are lauric acid, myristic acid, palmitic acid, stearic acid, tallow acid or mixtures of tallow acid and coconut acid, arachidic acid, behenic acid and lignoceric acid. Fatty acids are nonionic when utilized as the conglutinating agent. When the finished granules are utilized in alkaline solutions, however, the fatty acids are saponified to soap, an anionic surface active agent. Fatty acids having from 12 to 18 carbon atoms are preferred for use herein.

(8) Fatty alcohols containing from about 16 to about 30 carbon atoms which melt between 110° F. and 200° F. Specific examples of these nonionics are 1-hexadecanol, 1-octadecanol, 1-eicosanol, 1-heneicosanol, 3-docosanol, 1-tetracosanol and 1-octacosanol.

(9) Glycerides selected from the group consisting of monoglycerides, diglycerides, and mixtures thereof, which

melt between the temperatures of 110° F. and 200° F. Specific examples of these glycerides include 1,3-distearin, 1-monostearin, 1-monoarachidin, 1-monopalmitin, 1,3-dimyristin, 1-monocaprin and 1,3-dicaprin.

Many of these nonionic surface active agents are also detergents. Nonionic surface active agents other than those specifically mentioned herein but which have the properties hereinbefore described can be used in this invention. These ordinarily solid, low melting nonionics will protect the enzymes from degradation and function in the same manner as those specifically described above.

In the practice of the process of this invention, the ethoxylated acids and ethoxylated alcohols are especially preferred.

In a further preferred embodiment of this invention the total enzyme content, i.e., active enzymes or enzyme compositions, of a final granular detergent composition is provided by only a minor portion, i.e., from about 2% to about 30%, of the total granules therein. This 2–30% proportion are the finished granules described above. By affixing the enzymes to only a portion of the granules in a final detergent composition stability of the enzymes is further enhanced. Also, these enzyme-containing finished granules can be distinctively colored to provide a distinctive appearance for a final detergent composition in accordance with the teachings of Canadian Pat. 577,479, Britt. In this embodiment, from about 3% to about 10% of nonionic by weight of the base granules is preferably utilized to obtain finished granules.

Base granules, as hereinbefore described, are detergent granules to which enzymes can be attached. Finished granules are base granules having enzymes attached thereto. Base granules can be comprised solely of builder salts or they can contain a combination of builder salts and organic detergent compounds. The builder salts and organic detergent compounds and the ratios in which these components are utilized in base granules are more fully described hereinafter.

Organic detergents

The organic detergent compounds which can be utilized in the base carrier detergent granules and the final detergent compositions of this invention are the following:

(a) Water-soluble soap: Examples of suitable soaps for use in this invention are the sodium, potassium, ammonium and alkanolammonium (e.g., mono-, di-, and triethanolammonium) salts of higher fatty acids (C_{10}–C_{22}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

(b) Anionic synthetic non-soap detergents. A preferred class can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic, sulfuric acid reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of 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 (C_8–C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group can be a straight or branched chain and contains from about 9 to about 15 carbon atoms; sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium or potassium 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 about 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; sodium and potassium salts of sulfonated C_{10}–C_{24} α-olefins.

(c) Nonionic synthetic detergents. One class can be utilized in the detergent granules as detergent actives in addition to their specific function of rendering the detergent granules glutinous. The nonionics 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.

(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.

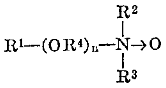
(2) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the said ethylene oxide being present in amounts equal 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 alcohol-ethylene 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

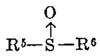


$$R^1-(OR^4)_n-\underset{R^3}{\overset{R^2}{N}}\rightarrow O$$

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 and bis(2-hydroxyethyl)dodecylamine 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 oxide are found in U.S. Pat. 3,304,263 which issued Feb. 14, 1967, and include: dimethyldodecylphosphine oxide and dimethyl-(2-hydroxydodecyl) phosphine oxide.

(8) Long chain sulfoxides having the formula



$$R^5-\overset{\overset{O}{\uparrow}}{S}-R^6$$

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

(d) Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical 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 24 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato or phosphono. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N - hexadecylammonio) - 2 - hydroxy propane-1-sulfonate which are preferred for their cool water detergency characteristics. See, for example, Snoddy et al., Canadian Pat. 708,148.

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

Builder salts

The base granules utilized in this invention also contain water-soluble, builder salts either of the organic or inorganic types. Enzymes may be degraded if maintained in sustained contact with aqueous solutions of these builders. However, the enzymes are protected from adverse intimate contact with these builders in the product and process of this invention.

Examples of suitable water-soluble, inorganic alkaline detergency builder salts are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates, silicates and sulfates. Specific examples of such salts are sodium and potassium tetraborates, perborates, bicarbonates, carbonates, tripolyphosphates, pyrophosphates, orthophosphates and hexametaphosphates. Sodium sulfate, although not classed as an alkaline builder salt, is included in this category.

Examples of suitable organic alkaline detergency builder salts are: (1) Water-soluble aminopolycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates and N-(2-hydroxyethyl)-nitrilo diacetates; (2) Water-soluble salts of phytic acid, e.g., sodium and potassium phytates—see U.S. Pat. 2,739,942; (3) Water-soluble, polyphosphonates, including specifically, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid, sodium, potassium and lithium salts of methylene diphosphonic acid, sodium, potassium and lithium salts of ethylene diphosphonic acid, and sodium, potassium and lithium salts of ethane-1,1,2 - triphosphonic acid. Other examples include the alkali metal 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; (4) Water-soluble salts of polycarboxylate polymers and copolymers as described in the copending application of Francis L. Diehl, Ser. No. 269,359, filed Apr. 1, 1963 now Pat. No. 3,308,067. Specifically, a detergent builder material comprising a water-soluble salt of a polymeric aliphatic polycarboxylic acid having the following structural relationships as to the position of the carboxylate groups and possessing the following prescribed physical characteristics: (a) a minimum molecular weight of about 350 calculated as to the acid form; (b) an equivalent weight of about 50 to about 80 calculated as to acid form; (c) at least 45 mole percent of the monomeric species having at least two carboxyl radicals separated from each other by not more than two carbon atoms; (d) the site of attachment to the polymer chain of any carboxyl-containing radical being separated by not more than three carbon atoms along the polymer chain from the site of attachment of the next carboxyl-containing radical. Specific examples are 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; and (5) mixtures thereof.

Mixtures of organic and/or inorganic builders can be used and are generally desirable. One such mixture of builders is disclosed in the copending application of Burton H. Gedge, Ser. No. 398,705, filed Sept. 23, 1964, now U.S. 3,392,121, e.g., ternary mixtures of sodium tripolyphosphate, sodium nitrilotriacetate and trisodium ethane-1-hydroxy-1,1-diphosphonate. The above described builders can also be utilized singly in this invention. Especially preferred builders that can be used singly or in combination in this invention include sodium perborate and sodium tripolyphosphate. Sodium tripolyphosphate and sodium perborate can be used in combination in a weight ratio range of from about 95:5 to about 50:50.

In the practice of this invention, it is especially preferred to use anhydrous and incompletely hydrated builder salts as described above in order to bind any free water which may come in contact with the finished granules and, thus, protect the enzymes from contact with solutions of concentrated alkaline products. The sodium and lithium salts of the above builders are generally preferred for this purpose as the cation of the hydratable builder salt can markedly affect the amount of water which can be bound as water of hydration to a single molecule. The sodium and lithium hydratable salts form more hydrates and form the hydrates more readily than do the ammonium, substituted ammonium and potassium salts. Hydratable salts suitable for use with enzymes are listed in concurrently filed copending application of Arnvid S. Roald and Nicholaas T. deOude.

Base carrier granules

The builder salts utilized in the base granules described herein should comprise from about 10% to about 100%, preferably from 10% to 90%, by weight of the base granules. Organic detergent compounds are generally and preferably included in these base granules. The ratio of builder salts to organic detergent compounds, hereinbefore defined, is preferably from about 1:4 to about 30:1, more preferably from about 0.4:1 to about 15:1.

The base granules of this invention can also contain minor amounts of other materials to make them more attractive or more effective. The following are mentioned by way of example. A soluble sodium carboxymethylcellulose may be added in minor amounts, e.g., 0% to about 5%, to inhibit soil redeposition. Tarnish inhibitors such as benzotriazole or ethylene-thiourea or phosphonate corrosion inhibitors such as those disclosed in the copending application of Roger E. Zimmerer, Ser. No. 577,149, filed Sept. 6, 1966, now U.S. 3,351,558, may also be added in amounts up to about 2%. Brighteners, fluorescers, bactericides, perfume and color may be added in amounts up to about 3%.

To avoid caking and/or segregation in the final detergent composition, the base granules and enzyme-free detergent granules making up a final detergent composition should have particle size distributions and densities which are approximately the same. The particle size distributions should be such that about 100% of the granules pass through a Tyler Standard 6 mesh screen and about 100% of the granules are retained on a Tyler Standard 200 mesh screen (i.e., ranging from about .075 mm. to about 3.3 mm. in particle size). Preferably, the particle size distribution should range from about 100% of the granules through a Tyler Standard 12 mesh screen to about 100% of the granules retained on a Tyler Standard 100 mesh screen (i.e., ranging in particle size from 0.14 mm. to 1.4 mm.). Another particularly useful size distribution is not more than 30% of the granules retained on a Tyler Standard 14 mesh screen and no more then about 7% of the granules through a Tyler Standard 100 mesh screen. The density of the granules making up the detergent composition should range from about 0.2 gm./cc. to about 0.8 gm./cc.

Preparation of base granules

Base granules can be formed in several ways. Detergent ingredients, such as builder salts and organic detergents, can be slurried and spray dried in a manner well known in the art. Anhydrous, partially hydrated and totally hydrated detergent granules can be obtained in this manner. The anhydrous and partially hydrated granules are preferred in this invention.

Other preferred base granules can be formed by agglomerating powders of detergent ingredients. Preferably at least one of these detergent ingredients is a hydratable builder salt. These hydratable salts will bind any moisture to which the finished granules are exposed, thus preventing solubilization of the alkaline builders which would attack the enzymes therein. Preferred agglomerating agents in this process for making base granules are the heretofore described glutinous nonionics, although other organic adhesives can be utilized. From about 3.0% to about 20% of nonionic or other adhesive by weight of the base granule ingredients are utilized in agglomeration. The adhesive is generally liquefied and sprayed onto an agitated mixture of the base granule ingredients. These agglomerated base granules can be formed in conventional agglomerating equipment such as a continuous mixer, e.g., a pan agglomerator or granulator, a revolving inclined drum, a cement mixer or a fluidized bed. Agglomerated base granules should be within the size ranges and density ranges hereinbefore specified.

Conglutination process

The firt step of this process involves rendering the surfaces of the base granules glutinous with an ordinarily solid, water-soluble, nonionic surface active agent which melts between 110° F. and 200° F. and is solid below temperatures of 110° F. It is desirable that the nonionic be solid at temperatures below 110° F. to prevent product stickiness and caking under ordinary storage conditions. The nonionic should, however, have a low enough melting point to avoid denaturing the enzyme when the tacky or sticky nonionic is contacted with the enzyme in the following step. Additionally, the nonionic should release the enzymes in water under ordinary pre-soak conditions, e.g., 75° F. and ordinary washing conditions, e.g., 130° F. The nonionic, in addition to acting as a binding agent, also lends surface activity to finished granules and increases their total detergency effectiveness.

In a preferred embodiment, the nonionic is liquified by heating it to between 110° F. and 200° F. and then sprayed on the base granules in Step 1. However, the nonionic can be contacted with the base granules in other ways well known in the art. From about 3.0% to about 90% preferably, from 5% to 15% of the above-described nonionic by weight of the base granules is used to render the granules glutinous or sticky. If agglomerated base granules, which are agglomerated with ordinary solid nonionics, are utilized no further nonionic need be contacted with the base granules. Such base granules which have been contacted with the nonionic are merely warmed to or are retained at a temperature slightly above that at which the nonionic will become sticky or glutinous. The surfaces of the granules will thus be rendered glutinous.

The second step of this process involves conglutinating, with the glutinous surface of the base granules, from about 0.001% to about 40% by weight of the finished granules of active enzymes, said enzymes being conglutinated in a powdered form. The enzymes can be active enzymes or enzyme compositions. When enzyme compositions are employed, the amount ranges from about 0.001% to about 60% by weight of the finished granules. In order to prevent damage to the enzymes, the base granules and the enzymes should be handled as gently as possible during this step.

Preferably, conglutination is performed on a pen agglomerator, i.e., a pan which can be rotated about an axis substantially different from the vertical. This inclined rotating pan furnishes a tumbling action which brings enzyme particles and base granules into intimate contact with each other to form finished granules. This tumbling action is gentle enough, however, so that the enzymes are not degraded. Conglutination of the enzymes and the base granules can also be performed with conventional agglomerating equipment such as continuous granulators, cement mixers, fludized beds or ribbon mixers.

Attaching the enzymes to the base granule by means of the nonionic reduces or prevents degradation of the enzymes by sustained contact with any alkaline and/or ionic substances in the base granule or detergent granules in the final detergent composition. In a preferred embodiment of this invention, from about 0.5% to about 5% by weight of the finished granules of additional nonionic is sprayed over the surface of the finished granules obtained from Step 2. This further application of nonionic at least partially encapsulates the enzymes and protects them further from contact with water, acid and alkaline substances and ionic detergents which might, on sustained contact, degrade the enzymes.

Conglutination and encapsulation can also be obtained in a two-step process. Liquid nonionic is sprayed onto a mixture of enzymes and base granules. When the nonionic becomes tacky or glutinous, the enzymes and base granules are conglutinated. Enzymes are wholly, or at least partially, encapsulated without an additional application of nonionic.

Conglutination and encapsulation can also be obtained by another process comprising the steps of mixing enzymes with warmed, liquid nonionic in the proportions hereinbefore specified and then spraying this mixture onto the base granules. Encapsulation of enzymes and conglutination of the enzymes and base granules is readily achieved by this method. This technique is one of the preferred process embodiments. In this preferred method, the pan agglomerator need not be employed.

By practice of the preferred processes, the enzyme-containing finished granules have a second coating of nonionic over the enzymes. In effect, the enzymes are totally or, at least, partially encapsulated and are further protected against degradation by contact with any highly alkaline substances employed in the final detergent compositions.

The products of this invention are effective in all cleaning applications in both hard and soft water. They are especially effective in removing soil and foreign materials from textiles and fabrics. For example, these products effectively remove or aid in removing 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, paint, grease, oil and grass stains. Additionally, by utilizing an enzyme which has some amylolytic activity, the final detergent compositions of this invention are particularly efficacious for dishwashing and cleaning pots and pans.

In addition to performing cleaning and whitening functions, the products of this invention facilitate measuring specific amounts of enzyme into a soaking or washing solution. This is advantageous since enzymes are effective in small amounts and are expensive when compared with ordinary detergents. By attaching the enzymes to base granules which serve as a diluent, the concentration of enzymes is decreased. Thus, the housewife can measure suitable amounts of product by effective amounts of enzymes into soaking or washing solutions.

Combinations of enzyme and per compounds having unexpected mildness

Another aspect of this invention concerns detergent compositions having improved mildness characteristics. These detergent compositions contain a combination of a per compound such as sodium perborate and an enzyme. Such mild compositions can comprise only a per compound such as sodium perborate and an enzyme; however, in the usual application, other detergent ingredients are added to this combination, e.g., organic detergent compounds and builder salts as hereinbefore described.

The addition of enzymes or per compounds such as sodium perborate to detergent compositions generally decreases the mildness of that detergent composition. Surprisingly, and quite unexpectedly, it has been found that when combinations of per compounds such as sodium perborate and enzymes described herein are added to a detergent composition, there is little or no noticeable change in the mildness characteristics of the detergent compositions. These rather harsh detergent ingredients apparently coact in some manner to produce a mild detergent composition having the beneficial cleaning properties of both the enzyme and the per compound.

All of the enzymes, both active enzymes and enzyme compositions hereinbefore described, can be utilized in this mild detergent composition. However, some of the enzymes which contain sulfhydryl groups or disulfide bonds, e.g. pepsin, trypsin, papain, lipase, diastase and urease, may be inactivated by high concentrations of the per compounds described herein. Proteases having optimum activity in the alkaline range which do not contain sulfhydryl groups or disulfide bonds are not inactivated to any great extent by these per compounds and are therefore highly desirable for use in this mild detergent composition. The proteases having optimum activity in the alkaline range which do not contain sulfhydryl groups or disulfide bonds are exemplified by the subtilisin family of enzymes, for example, BPN', Novo Bacterial Proteinase, Alcalase and the alkaline protease portion of CRD protease hereinbefore described.

The active enzyme content of the mild detergent composition should, preferably, be from about 0.005% to about 4.0% by weight of the detergent composition, and most preferably, from about 0.006% to about 0.12%.

The per compounds utilized in this aspect of this invention comprise, preferably, from about 5% to about 30% of the mild detergent composition, most preferably, from about 8% to about 25%. Other per compounds can be used instead of the preferred sodium perborate, e.g., sodium percarbonate and sodium persulfate. Other cations can be utilized in place of sodium, e.g., potassium, ammonium and lithium.

The remainder of the mild detergent composition can be comprised of active detergent compounds and builder salts in the hereinbefore described ratios.

These mild detergent compositions can be made by mechanically mixing, by the process described herein or by the process described in copending application, Ser. No. 620,603 filed concurrently by Roald et al., or by any of the detergent preparation methods known in the art.

The mild detergent composition of this invention can be used in a broad spectrum of cleaning applications. When these mild detergent compositions are formulated by excluding anionic detergents, they are especially useful in removing large amounts of blood from fabrics and particularly in preventing discoloration of the fabric by redeposition of the blood on the fabric. A specific example of the utility of this detergent composition is in removal of menstrual blood from sanitary cloths. When these particular detergent compositions are utilized for cleaning blood-soaked fabrics, further bleaching is generally not required in order to obtain bright and/or white fabrics.

The anionic detergents are excluded from the above-described detergent compositions to prevent haemolysis or destruction of the red blood cells. The anionic detergents apparently destroy the red blood cells much more quickly and more thoroughly than do the nonionic and zwitterionic detergents. While not wishing to be bound by any particular theory, it is believed that the contents of the red blood cells are primarily responsible for discoloration of the fabric because of redeposition of the cell contents on the fabric.

The organic detergents used in the mild detergent compositions in this particular application should be selected from the group consisting of nonionic detergents and zwitterionic detergents. The nonionic detergents generally prevent redeposition of blood better than the zwitterionic detergents and are, therefore preferred. Preferred nonionic detergents include:

(1) Condensation products of one mole of a saturated or unsaturated, straight or branched chain carboxylic acid having from 10 to 18 carbon atoms with from about 3 to about 50 moles of ethylene oxide (see column 16 of the specification for some specific examples);

(2) Condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohol having from 10 to 24 carbon atoms with from about 3 to about 50 moles of ethylene oxide (see column 16 of the specification for some specific examples);

(3) Polyethylene oxide condensates of alkyl phenols (described in column 17 of the specification);

(4) Long chain tertiary amine oxides (described in column 17 of the specification); and

(5) Long chain tertiary phosphine oxides (described in column 17 of the specification.

The per compounds and enzymes can be used in this detergent composition in amounts delineated hereinbefore. Proteases are the preferred enzymes for this particular application; however, other enzymes can also be utilized in combination with the proteases to obtain a detergent composition having a broader use potential. Builder salts as hereinbefore described are generally, and preferably, included in the finished formulation. The builder salts and organic detergents for this particular application are used in the ratios defined hereinbefore. In its simplest form, this specific mild detergent composition having special advantages in removing large amounts of blood from fabrics and being substantially free of anionic detergents comprises:

(1) nonionic or zwitterionic detergents,
(2) per compounds,
(3) enzymes, and generally
(4) builders.

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 they are not intended to restrict the invention.

In the examples, enzymatic activity is determined by the Azocoll method which 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 I

Four pounds of powdered sodium perborate

$$(NaBO_2 \cdot 3H_2O \cdot H_2O_2)$$

were placed in a baffled laboratory cement mixer and the cement mixer was turned on. A quantity of the condensation product of coconut alcohol having a carbon chain length distribution of 2% C_{10}, 66% C_{12}, 23% C_{14} and 9% C_{16} and 45 moles of ethylene oxide ($CNAE_{45}$) was heated to 135° F. at which point the $CNAE_{45}$ was entirely liquefied. About 0.2 pound of $CNAE_{45}$ were sprayed onto the powdered perborate which was tumbling in the cement mixer. The $CNAE_{45}$ made the perborate powder sufficiently sticky or glutinous to cause the formation of perborate granules having a particle size ranging as follows: 25.4% on Tyler Standard 14 mesh screen, 56.4% on Tyler Standard 20 mesh screen; 86.4% on Tyler Standard 35 mesh screen; 95.5% on Tyler Standard 65 mesh screen and 98.9% on Tyler Standard 100 mesh screen. The density of these granules was 0.5 gm./cc.

As the outside surfaces of the granules were still tacky, no additional spray-on of nonionic detergent was required. Two pounds of Alcalase, as hereinbefore described, were added to the cement mixer. The bulk temperature inside the cement mixer was about 110° F. The mixer was left on for about ten minutes at which time the enzyme, i.e., Alcalase, was firmly attached to the outside surfaces of the detergent granules. The bulk temperature at this time was 105° F.

The granules were allowed to cool to about 80° F. and were then coated with an additional 0.1 pound of $CNAE_{45}$. This coating was applied by placing the enzyme-containing detergent granules in the cement mixer, turning it on and then spraying the liquid $CNAE_{45}$ at a temperature of about 135° F. onto the granules. After the nonionic solidified, a small amount of blue dye was sprayed on these granules to color them a bright blue. A mixture of 1.5 pounds of these blue granules, 23 pounds of granular sodium tripolyphosphate having a density of about 0.5 gms./cc., and 25 pounds of sodium perborate: $CNAE_{45}$ granules (95% perborate, 5% $CNAE_{45}$) having a density of 0.5 gm./cc. was then prepared which was suitable for use as a laundry additive product. The final product was granular and free flowing. The enzyme-containing particles did not segregate in the final product.

This formulation has a density of about 0.5 gm./cc. and contains about 0.06% active enzyme, i.e., about 1% Alcalase. The recommended usage level of this product in ordinary laundry washing is one-half cup per wash. When this product was utilized in an ordinary washing cycle in addition to one cup of a commercial detergent product, i.e., Tide, naturally soiled clothes were given an enhanced whiteness and, likewise, soil removal was enhanced. It was mild to the skin.

This product was stored under various conditions for one week and then the active enzyme content of the stored product was compared with the product just after conglutination. When the product was stored at 50° F. for one week, the active enzyme content was 98% as compared with the product just after conglutination. When the product was stored at 80° F. for one week, the active enzyme content was 97%. When the product was stored in an environment which was maintained for alternate twelve hour periods at 50° F. and 100° F. for one week, the active enzyme content was 87%. Only minor amounts of enzyme activity were lost by the product produced by the process of this invention.

EXAMPLE II

A granular spray-dried detergent composition having a particle size ranging from about 6% retained on a Tyler Standard 14 mesh screen to about 1.8% through a Tyler Standard 100 mesh screen and having a bulk density of 0.35 gm./cc. is prepared from the following ingredients:

	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_{12}, 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 ammonia amide wherein the acyl group contains from 12 to 16 carbon atoms	2.5
Sodium sulfate	14.0
Water	10.0

The various ingredients are slurried in an ordinary detergent crutcher and then spray dried. Twenty pounds of these detergent granules are slowly fed into a pan agglomerating unit. One pound of liquid $CNAE_{45}$ at 135° F. is sprayed uniformly over the surface of these detergent granules while the pan is turning at 12 revolutions per minute. When the surfaces of the granules are uniformly covered by the $CNAE_{45}$, the rotating pan is turned off. The granules are allowed to remain at room temperature until the $CNAE_{45}$ becomes sticky or glutinous. At this time, the pan agglomerator is again turned on and five pounds of Alcalase as hereinbefore defined are added to the pan agglomerator. The pan agglomerator is allowed to run for seven minutes, at which time all of the Alcalase is uniformly attached to the detergent granules. The granules are retained at room temperature for 40 minutes, at which time they are placed in a cement mixer. One pound of $CNAE_{45}$ is sprayed on these detergent granules. The final product is free flowing.

The Alcalase can also be attached to the detergent granules above-described by spraying a slurry of Alcalase and $CNAE_{45}$ on these granules. Two pounds of $CNAE_{45}$ are heated to 150° F. and maintained in a liquid state. One pound of Alcalase is uniformly mixed into the liquefied nonionic. This mixture is immediately sprayed onto

20 pounds of the detergent granules whereby, simultaneously, the base detergent granules are rendered glutinous, the enzymes are conglutinated with the base granules and the enzymes are encapsulated. The finished detergent composition is allowed to cool to prevent caking. The composition is free flowing and suitable for use as a heavy-duty laundry detergent.

Enzymes can also be attached to the base detergent granules in another way. In this example, a uniform mixture of 50 parts of Alcalase, and 50 parts of sodium tripolyphosphate granules is prepared. Eighty-four grams of $CNAE_{45}$ was heated to about 140° F. and then sprayed uniformly over the surfaces of 333 grams of the mixture of Alcalase and sodium tripolyphosphate. The nonionic became tacky in a very short time, i.e., about 10 seconds. When the nonionic had reached this tacky state, the glutinous particles were fed into a pan agglomerator in which granules meeting the size requirements hereinbefore mentioned were formed. No additional spray-on of nonionic was required to encapsulate the enzymes as the enzymes were encapsulated during the initial nonionic spray-on. By this method, the base granules, as well as the enzyme particles, are rendered glutinous and the enzyme particles are encapsulated in a single step.

EXAMPLE III

A soak detergent product was prepared which had excellent cleaning and whitening characteristics and which, in addition, substantially prevented degradation of the enzymes contained in said product. Base detergent granules were prepared by agglomerating, in a pan agglomerator, 2.16 parts of powdered, anhydrous sodium tripolyphosphate with 0.24 part of the condensation product of 1 mole of tallow fatty alcohol with 30 moles of ethylene oxide (TAE_{30}). Before the TAE_{30} was added to the sodium tripolyphosphate, it was liquefied by warming it to 140° F. The average bulk density of the base granules was about 0.5 gm./cc. The particle size distribution of the base granules was as follows:

Tyler standard screen size:	Percent on
14	0
20	1.5
28	8.4
35	14.1
58	33.0
65	24.0
100	14.0
Through 100	5.0

While the base granules were still warm and the TAE_{30} was still glutinous, 1.2 parts of Alcalase were conglutinated with the base granules to form finished granules. The finished granules were cooled to about 80° F., at which time about 0.12 parts of liquid TAE_{30} were sprayed uniformly over the surfaces of the finished granules to effect encapsulation of the Alcalase.

3.72 parts of the finished granules were mixed with 96.38 parts of granules having the following composition:

Component:	Parts by weight
Sodium Tripolyphosphate (anhydrous)	70.0
Sodium perborate agglomerates comprising:	
Sodium perborate	25.0
TAE_{30}	3.5

These granules had a particle size ranging from 100% through a Tyler Standard 12 mesh screen to 97% retained on a Tyler Standard 100 mesh screen. The bulk density was about 0.5 gm./cc.

This product was packaged and stored at 80° F. and ambient humidity for seven weeks. During the entire seven weeks there was essentially no loss in enzymatic activity. In another test where Alcalase was dry-mixed with the above described detergent composition and packaged in the same manner, there was about a 30% loss in enzymatic activity in a six week period. These tests demonstrate that the enzymes are protected by utilizing the conglutination method of this invention. No segregation problems were apparent.

The product of this example was primarily designed as a soaking product. Excellent cleaning and whitening benefits are obtained with this product. It had improved mildness to the skin.

EXAMPLE III(A)

A granular, spray-dried detergent composition having a particle size ranging from about 10% through a Tyler Standard 12 mesh screen to about 100% on a Tyler Standard 100 mesh screen and having a bulk density of about 0.35 gm./cc. is prepared having the following composition:

	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_{12}, 35% C_{13} and 22% C_{14}	10
Sodium tripolyphosphate	75
Sodium sulfate	10
Water	5

About 4% Alcalase by weight of the base granules is dry-mixed with the above-described base granules. About 8% of tallow fatty acid by weight of the base granules is heated to its melting point and sprayed onto the mixture of base granules and enzymes. The base granules and enzymes are then conglutinated in a pan agglomerator according to the procedure followed in the last paragraph of Example II.

The finished granules resulting from the above process were then mixed with 90 parts of a Detergent I. Detergent I is a granular spray-dried detergent composition having a particle size ranging from about 100% through a Tyler Standard 12 mesh screen to about 100% on a Tyler Standard 100 mesh screen and having a bulk density of about 0.35 gm./cc. and having a composition as follows:

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_{12}, 35% C_{13} and 22% C_{14}	17.05
Sodium tripolyphosphate	50.0
Sodium silicate having an $SiO_2:Na_2O$ ratio of 1.8:1	6.0
Coconut ammonia amide wherein the acyl group contains from 12 to 16 carbon atoms	2.5
Sodium sulfate	14.0
Water	10.0

This product is packaged and stored for protracted periods of time. There is essentially no loss of enzymatic activity during the first 30 days. In detergent compositions having similar compositions except that Alcalase is dry-mixed with the detergent composition, loss of enzymatic activity is substantial in a 30 day period.

Results substantially similar to those achieved above and in the previous examples are obtained when other ordinarily solid, nonionic surface active agents melting between the temperatures of 110° F. and 200° F. are substituted for the tallow fatty acid of Example III(A) in that the base detergent granules are rendered glutinous, the enzymes are attached thereto and encapsulated and the stability of the enzymes is enhanced. These other nonionics include: lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, 1-hexadecanol, 1-octadecanol, 1-eicosanol, 1-heneicosanol, 3-docosanol, 1-tetracosanol, 1-octacosanol, 1,3-distearin, 1-monostearin, 1-monoarachidin, 1-monopalmitin, 1,3-dimyristin, 1-monocaprin, 1,3-dicaprin.

EXAMPLE IV

Results substantially similar to those in the previous examples are obtained when other enzymes are substituted, either wholly or in part, for Alcalase in that the resulting product enhances soil removal and improves whiteness maintenance. The commercial enzyme compositions that are substituted for Alcalase to obtain the surprising results of this invention are Maxatase, Protease B–4000, Sandoz 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, Rhozym J–25, Amprozyme 200. Other active enzymes which are substituted for Alcalase including pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, ficin, subtilisin, BPN′, papain, bromelin, carboxylase, amino peptidase, aspergillopeptidase A, aspergillopeptidase B, gastric lipase, pancreatic lipase, plant lipases, phospholipases, cholinesterases, phosphotases, maltase, saccharase, amylase, cellulase, pectinae, lysozyme, α-glycosidase, β-glycosidase, ribonuclease and desoxy ribonuclease.

All of these enzymes described herein are utiized in this invention in a dry, powdered form. The particle size diameters of the enzymes utilized herein are such that most of the particles will pass through a Tyler Standard 20 mesh screen. A major portion of the enzyme particles usually remain on a Tyler Standard 150 mesh screen.

EXAMPLE V

Results substantially similar to those achieved in the previous examples are obtained when other ordinarily solid, water-soluble, nonionic surface active agents melting between the temperatures of 110° F. and 200° F. are substituted for the nonionic surface active agents hereinbefore utilized in that the resulting product enhances soil removal and improves whiteness maintenance. When in the above examples, the following nonionic surface active agents are substituted, either wholly or in part for those nonionics, substantially similar results are obtained in that the base detergent granules are rendered glutinous, the enzymes are attached thereto and the enzymes are encapsulated: the condensation product of one mole of coconut fatty acid having the approximate chain length distribution of 2% C_{10}, 66% C_{12}, 23% C_{14} and 9% C_{16} with 35 moles of ethylene oxide; the condensation product of one mole of palmitic acid with 40 moles of ethylene oxide; the condensation product of one mole of myristic acid with 35 moles of ethylene oxide; the condensation product of one mole of oleic acid with 45 moles of ethylene oxide; and the condensation product of one mole of stearic acid with 30 moles of ethylene oxide; the condensation product of one mole of 2-methyl tetradecanoic acid with 45 moles of ethylene oxide; the condensation product of one mole of tallow alcohol with 20 moles of ethylene oxide; the condensation product of one mole of lauryl alcohol with 35 moles of ethylene oxide; the condensation product of one mole of myristic alcohol with 30 moles of ethylene oxide; the condensation product of one mole of 2-methyl tetradecanol with 45 moles of ethylene oxide; the condensation product of one mole of oleyl alcohol with 40 moles of ethylene oxide; polyoxyethylene glyceride esters, having a hydrophile-lipophile balance of about 18:1; polyoxyethylene lanolin derivatives having a hydrophile-lipophile balance of about 17.0; polyethylene glycols having a molecular weight of from about 1400 to about 30,000, e.g., 20,000, 9,500, 7,500, 4,500, 3,400, 1,450; the condensation products of one mole of alkyl phenol wherein the alkyl chain contains 8, 10, 12, 15, 16 or 18 carbon atoms with 25, 35, 45 or 50 moles of ethylene oxide; water-soluble amides having a melting point between 110° F. and 200° F., e.g., propyl amide, N-methyl amides having an acyl chain length of 10, 12, 14 or 15 carbon atoms, pentyl anilide and anilides having a carbon chain length of 7, 8, 10 or 12 carbon atoms, oleamide, amides of ricinoleic acid, N-isobutyl amides of pelargonic acid, capric acid, undecanoic acid and lauric acid, N-(2-hydroxy ethyl) amides having carbon chain

lengths of 6, 8 or 10 carbon atoms, N-cyclopentyllauramide and N-cyclopentylstearamide.

EXAMPLE VI

When the following hydratable builder salts or mixtures thereof are substituted, either wholly or in part, for the builders in the previous examples, substantially equivalent results are obtained in that the enzymes are protected from any water which enters the packaged detergent composition: tripolyphosphates; sulfates; carbonates; pyrophosphates; phosphates; hexametaphosphates; ethylenediaminetetraacetates; N-(2-hydroxyethyl)-ethylenediaminetriacetates; nitrilotriacetates; N-(2-hydroxyethyl)-nitrilodiacetates; phytates; ethane-1-hydroxy-1, 1-diphosphonates; ethane-1,1,2-triphosphonates; ethane-2-carboxy-1,1-diphosphonates; hydroxymethanediphosphonates; carbonyldiphosphonates; ethane-1-hydroxy-1,1,2-triphosphonates; propane-1,1,3,3-tetraphosphonates; methylene diphosphonates; and ethylidene, isopropylidene and benzylmethylidene, in the form of their sodium, potassium, lithium, triethanolammonium, diethanolammonium and monoethanolammonium salts. The sodium salts demonstrate the best properties for use in this invention. The hydratable builder salts used herein 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 and, 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. These hydratable builder salts have average bulk densities ranging from 0.2 gm./cc. to 0.8 gm./cc., e.g., 0.5 gm./cc.

EXAMPLE VII

When the following active detergents are included or substituted, either wholly or in part for the detergent substances in the previous examples, substantially similar results are obtained: sodium coconut soap, sodium linear alkyl benzene sulfonate having a chain length distribution of 10% C_{10}, 30% C_{11}, 35% C_{12}, 16.5% C_{13}, 8% C_{14} and 0.5% C_{15}, 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; coconut diethanol amide; dimethyldecylamine oxide; cetyldimethylphosphine oxide; sodium-3-dodecylaminopropionate; and 3-(N,N-dimethyl-N-hexadecylammino) propane-1-sulfonate.

EXAMPLE VIII

Spray-dried, granular detergent compositions were prepared, comprised of the following components:

	Parts by weight			
	Detergent A		Detergent B	
	1	2	1	2
Sodium perborate		9.1		9.1
Sodium tetrapropylene benzene sulfonate	7.8	7.8	19.5	19.5
Sodium tripolyphosphate	65.0	65.0	35.5	35.5
Sodium silicate			7.1	7.1
Sodium sulfate	14.7	14.7	15.7.	15.7
Water	9.0	9.0	5.9	5.9

To each of the above detergents, A(1), A(2), B(1) and B(2), 0.774 part of enzyme composition were added. The enzyme composition utuilized in detergents A(1) and A(2) was Maxatase while both Alcalase and Maxatase were separately utilized on a pro rata basis in separate portions of detergents B(1) and B(2). The enzyme compositions were merely dry-mixed with the detergent compositions. Immediately after mixing these compositions were utilized in the hand immersion tests of this example.

The tests illustrated hereinafter are designed to show the relative mildness of the detergent compositions set forth above. A 2% solution of these detergent compositions is prepared. The water is maintained at 110° F. The test subjects place one hand in the above-described solution for 30 minutes on each of four successive days. On the fifth day, the subjects' hands are examined.

The concentrated solutions, long immersion times and hot water are quite exaggerated testing conditions and are utilized to produce some irritative symptoms in order to facilitate grading of relative mildness. The irritative symptoms that may be observed are:

(1) Irritable redness—(All of the products utilized in this test caused some irritable redness of the wrists because of the high concentration of detergents and the long immersion times.)

(2) Slight rash—(This rash consisted of very minute spots which were hardly noticeable. In most cases, the rash disappeared quickly but in a few cases, the rash persisted.)

(3) Heavy rash.

The first test was run utilizing detergents A(1) and A(2). The detergents were the same except for the inclusion of sodium perborate in detergent A(2). Two percent solutions of detergents A(1) and A(2) were prepared with 110° F. water. Sixty-four subjects were utilized in these tests, 32 in each separate test, with each subject placing one hand in the solutions for 30 minutes on each of four successive days. On the fifth day, the test hand of each subject was graded.

No irritative symptoms, i.e., slight or heavy rash, were observed on the hands of the subjects using detergents A(2). Two of the subjects using detergent A(1) suffered from a heavy rash on their hands.

Similar tests under similar conditions were run with detergents B(1) and B(2). The results of these tests are tabulated below:

	Detergent B(1)								Detergent B(2)							
	Alcalase				Maxatase				Alcalase				Maxatase			
Total hands	13				16				14				16			
Immersions	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Slight Rash (No. of subjects)		6	X	X		2	X	X			1	1				1
Heavy Rash		2	X	X		4	X	X								1

In the tests utilizing detergent B(1) with Maxatase and with Alcalase, the hand immersions were stopped after the second immersion because of the high irritancy potential of this solution (X=no reading). With Alcalase, 6 of the 13 subjects suffered from a slight rash and 2 suffered from a heavy rash. With Maxatase, 2 of the 16 subjects suffered from a slight rash and 4 from a heavy rash after the second immersion. When perborate was added to the system, i.e., detergent B(2), and four successive immersions utilized, only 2 subjects out of 14 suffered from a slight rash and none from a heavy rash when Alcalase was included in the detergent composition. When Maxatase was utilized, 1 subject out of 16 suffered from a slight rash and 1 suffered from a heavy rash.

A comparison of the test results using detergents B(1) and B(2) shows that the combination of enzyme and sodium perborate in detergent compositions is strikingly more mild than enzymes alone in detergent compositions. It further shows a synergistic mildness combination of sodium perborate and enzymes.

EXAMPLE IX

Detergent compositions, A and B, were prepared. In both cases, all the components, except the enzymes, were mixed together in an aqueous slurry and then spray-dried. The enzymes were dry-mixed with the spray-dried granules.

	Parts by weight	
	Component A	Component B
Sodium tripolyphosphate	40	40
Sodium linear alkyl benzene sulfonate (see Example II)	16	16
Sodium sulfate	24	14
Sodium perborate		10
Sodium silicate	6	6
Water	10	10
Alcalase	1	1
Miscellaneous	(to 100 parts)	

Separate detergent solutions were prepared, each day of this test, utilizing detergents A and B. The detergents were used in concentrations of 2% in water which was maintained at 100° F. This product concentration is considerably higher than that used for most cleaning jobs.

To determine the relative mildness of these two detergent compositions, six subjects immersed their hands, one in each solution, for one-half hour per day on successive days. The subjects' hands were graded on a scale from 1 to 10. A score of 10 indicated no reaction to the solutions. A score of 1 was a very violent reaction. All tests were stopped when one hand reached a grade of about 7 which indicates a moderate reaction, i.e., redness and, in some cases, a slight rash. Both hands were graded at this time and, if one hand was significantly better (one grade point in this test is a significant difference) than the hand graded as 7, that hand was reimmersed until a grade of 7 was obtained.

The following table shows the average grade of hands immersed in solutions of detergents A and B and the average number of immersions required to reach a grade of 7.

Detergent	Average immersions required to reach about Grade 7 (immersions equal one-half hour)	Average grade of both hands when one hand reaches about Grade 7
A	2.8	7.3
B	3.8	8.7

In all cases, detergent B (perborate plus enzymes) was milder than detergent A. Hands immersed in detergent A reacted to the detergent composition more quickly and reacted more unfavorably than did hands immersed in detergent B. A comparison of the test results above shows that the combination of enzymes and sodium perborate in detergent compositions is more mild than enzymes alone in detergent compositions.

EXAMPLE X

A granular spray-dried detergent composition having a particle size ranging from about 6% retained on a Tyler Standard 14 mesh screen to about 1.8% through a Tyler

Standard 100 mesh screen and having a bulk density of 0.35 gm./cc. is prepared from the following ingredients:

	Percent 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_{12}, 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 ammonia amide wherein the acyl group contains from 12 to 16 carbon atoms	2.5
Sodium sulfate	14.0
Water	10.0

This detergent composition is separated into four separate portions and sodium perborate and enzymes are added as shown below.

	Percent			
Additions by weight of detergent composition	I	II	III	IV
Sodium perborate			10	10
Alcalase		0.8		0.8

Detergents II and III are considerably less mild than the control, Detergent I, while Detergent IV containing the combination of Alcalase and sodium perborate is as mild as the control. This test shows, again, the synergistic mildness combination of sodium perborate and enzymes, specifically, Alcalase.

EXAMPLE XI

Results substantially similar to those in Examples VIII, IX and X are obtained when other per compounds are substituted, either wholly or in part, for sodium perborate in that the resulting product is surprisingly mild. The per compounds that can be substituted for sodium perborate include the sodium, potassium, lithium and ammonium persulfates, percarbonates and perborates.

EXAMPLE XII

A menstrual blood solution was prepared by soaking several used sanitary napkins in water at room temperature (80° F.) for two hours. 0.4% of detergent composition by weight of the menstrual blood solution was added. The detergent composition comprised:

	Percent
Organic detergent (as shown below)	22
Sodium tripolyphosphate	55
Sodium perborate	22
Alcalase	1

Clean, white muslin swatches were soaked in the blood/detergent composition solution for about 16 hours. The swatches were then rinsed with clear water, dried and measured for color on an EEL Reflectometer. The EEL units in the following table indicate the amount of redeposition with 0 units indicating a cloth with no redeposition. A difference of 2 EEL units is noticeable to the unpracticed eye.

The EEL Reflectometer used herein is comprised of a spectrophotometer head using a No. 602 filter coupled with a Unigalvo type 20 meter. The reflectometer is built by Evans Electroselenium Ltd., Sussex, England.

TABLE I.—BLOOD REDEPOSITION USING NONIONIC AND ANIONIC DETERGENT COMPOSITIONS

Percent sodium linear alkyl (C_{12}) benzene sulfonate (LAS)	Percent condensation product of one mole of tallow alcohol and 11 moles of ethylene oxide (TAE_{11})	Cloth color EEL reading[1]
	22	16
11	11	34
22		34

[1] Units darker than original muslin cloth.

As can be seen from the above table, redeposition of blood on the fabric is significantly increased by using an anionic detergent. When TAE_{11}, a nonionic detergent, was the only organic detergent present in the detergent composition, the EEL reading was 16. An EEL reading of 34 was obtained when 50% of the TAE_{11} was replaced with LAS, an anionic detergent. The difference of 18 EEL units between the cloths represents a significant color differential.

When the following nonionic detergents are substituted for TAE_{11}, the results are similar to those tabulated above in that there is less redeposition of blood on the fabric when nonionic detergents are the sole organic detergent in the detergent composition than when anionic detergents are utilized in the detergent composition: dimethyl dodecyl phosphine oxide; dimethyl dodecyl amine oxide; the condensation product of one mole of tallow alcohol and 30 moles of ethylene oxide; the condensation product of one mole of coconut alcohol with 5.5 moles of ethylene oxide.

When the following anionic detergents are substituted for LAS, substantially the same results are obtained as tabulated above:

Sodium branched chain alkyl (C_{12}) benzene sulfonate
20% sodium coconut soap, 80% sodium tallow soap
Coconut alkyl sulfate
Tallow alkyl sulfate

The foregoing description of the invention has been presented describing certain operable and 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. The process of making free-flowing, enzyme-containing, detergent granules consisting essentially of the steps of:

(1) rendering the surfaces of base carrier detergent granules, having a particle size distribution such that about 100% of the granules pass through a Tyler Standard 6 mesh screen and about 100% of the granules are retained on a Tyler Standard 200 mesh screen and having an average bulk density of from about 0.2 gm./cc. to about 0.8 gm./cc. glutinous with from about 3 percent to about 90 percent by weight of said base granules of a low melting, ordinarily solid, water-soluble nonionic surface active agent which liquefies between the temperatures of from about 110° F. to about 200° F. and which is solid at temperatures below 110° F.; and

(2) conglutinating with said glutinous surfaces of said base granules to form finished detergent granules from about 0.001 percent to about 40 percent by weight of the finished granules of active enzymes, said enzymes being conglutinated in a powdered form selected from the group consisting of active enzymes and enzyme compositions, said enzyme compositions, when employed, comprising from abou 0.001% to about 60% by weight of the finished granules, and said active enzymes being active in the pH range of from about 4 to about 12 and the temperature range of from about 50° F. to about 150° F.

2. The process of claim **1** wherein the enzymes are active in the pH range of from about 7 to about 11 and the temperature range of from about 70° F. to about 140° F. and wherein the enzyme is a hydrolase selected from the group consisting of proteases, esterases, carbohydrases and nucleases.

3. The process of claim **1** wherein said enzymes are in the form of an enzyme composition which is a proteolytic enzyme composition containing about 6% active enzyme derived from *Bacillus subtilis* and the remainder being essentially sodium sulfate and calcium sulfate.

4. The process of claim **1** wherein the base detergent granules comprise from about 10% to about 90% of builder salts.

5. The process of claim **4** wherein the cation of said builder salts is selected from the group consisting of sodium and lithium.

6. The process of claim **4** wherein the builder salts are incompletely hydrated.

7. The process of claim **4** wherein the builder salts are anhydrous and are selected from the group consisting of sodium tripolyphosphate and sodium perborate.

8. The process of claim **1** wherein the base detergent granules comprise builder salts and organic detergents selected from the group consisting of soap, anionic non-soap detergents, nonionic, ampholytic and zwitterionic detergents in a ratio of builder salts to organic detergents of from about 1:4 to about 30:1.

9. The process of claim **8** wherein the ratio of builder salts to organic detergents is from about 0.4:1 to about 15:1.

10. The process of claim **1** wherein from about 5% to about 15% of said nonionic surface active agent by weight of the base granules is utilized and is selected from the group consisting of the condensation products of aliphatic, saturated or unsaturated, straight or branched chain, carboxylic acids having from about 10 to 18 carbon atoms with from 20 to about 50 moles of ethylene oxide; the condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohol having from about 10 to about 24 carbon atoms with from about 10 to about 50 moles of ethylene oxide; polyoxyethylene glyceride esters having a hydrophile-lipophile balance of about 18.1; polyoxyethylene lanolin derivatives having a hydrophile-lipophile balance of about 17.0; polyethylene glycols having a molecular weight of from about 1400 to about 30,000; the condensation products of one mole of alkyl phenol wherein the alkyl chain contains from about 8 to about 18 carbon atoms with from about 25 to about 50 moles of ethylene oxide; water-soluble amides having a melting point between 110° F. and 200° F.; fatty acids containing from about 12 to about 30 carbon atoms; fatty alcohols containing from about 16 to about 30 carbon atoms; glycerides selected from the group consisting of monoglycerides, diglycerides and mixtures thereof which melt between the temperatures of 110° F. and 200° F.

11. The process of claim **10** wherein said nonionic liquefies between the temperatures of from about 120° F. to about 150° F. and is selected from the group consisting of the condensation products of saturated or unsaturated, straight or branched chain acids having from about 10 to about 18 carbon atoms with from about 20 to about 50 moles of ethylene oxide; and the condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohol having from about 10 to about 24 carbon atoms with from about 10 to about 50 moles of ethylene oxide.

12. The process of claim **1** wherein the finished detergent granules are encapsulated with from about 0.5% to about 5% by weight of the finished granules of the low-melting, ordinarily solid, water-soluble, nonionic surface active agent of claim **1** and wherein the base detergent granules have a particle size distribution such that about 100% of the base granules pass through a Tyler Standard 12 mesh screen and about 100% of the base granules are retained on a Tyler Standard 100 mesh screen.

13. The process of claim **1** wherein the base granules are rendered glutinous by:

(1) heating said nonionic surface active agent to a temperature of between 110° F. and 200° F. and thereby liquefying said nonionic; and

(2) spraying said nonionic surface active agent onto said base granules.

14. The process of claim **12** wherein, simultaneously, said base detergent granules are rendered glutinous with said nonionic and said enzymes are encapsulated with said nonionic comprising the steps of:

(1) preparing a mixture of said base detergent granules and said enzymes;

(2) heating said nonionic surface active agent to a temperature of between 110° F. and 200° F. and thereby liquefying said nonionic; and

(3) spraying said nonionic surface active agent onto said mixture of base detergent granules and enzymes.

15. The process of claim **1** wherein, simultaneously, said base granules are rendered glutinous, said enzymes are conglutinated with said base granules and said enzymes are encapsulated by the steps of:

(1) heating said nonionic surface active agent to a temperature of between 110° F. and 200° F. and thereby liquefying said nonionic;

(2) mixing said enzymes into said liquefied nonionic; and

(3) spraying the mixture of step 2 onto said base detergent granules.

16. Enzyme-containing detergent granules consisting essentially of:

(1) inner-core base carrier granules having a particle size distribution such that about 100% of the granules pass through a Tyler Standard 6 mesh screen and about 100% of the granules are retained on a Tyler Standard 200 mesh screen and having an average bulk density of from 0.2 gm./cc. to about 0.8 gm./cc.;

(2) a coating on said inner-core base granules of from about 5% to about 15% by weight of said inner-core base granules of a low-melting, ordinarily solid, water-soluble, nonionic surface active agent which liquefies between the temperatures of from about 110° F. to about 200° F. and which is solid at temperatures below 110° F.;

(3) from about 0.001% to about 40% of active enzymes by weight of the finished granules, said enzymes being in a powdered form selected from the group consisting of active enzymes and enzyme compositions, said enzyme compositions, when employed, comprising from 0.001% to 60% by weight of the finished granules, conglutinated on said inner-core base granules, said enzymes being active in the pH range of from about 4 to about 12 and the temperature range of from about 50° F. to about 150° F.

17. The enzyme-containing detergent granules of claim **16** wherein:

(1) the inner-core base granules have a particle size distribution 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; and

(2) the nonionic surface active agent liquefies between the temperatures of from about 120° F. to about 150° F.

18. The enzyme-containing granules of claim **16** having an outside coating of from about 0.5% to about 5% by weight of the finished granules of a low-melting, ordinarily solid, water-soluble, nonionic surface active agent, which liquefies between the temperatures of from about 110° F. to about 200° F. and which is solid at temperatures below 110° F., said coating being applied over the enzymes conglutinated on said nonionic coating on said inner-core base granules.

19. The enzyme-containing detergent granules of claim **16** wherein the inner-core base granules are comprised of anhydrous sodium tripolyphosphate.

20. The enzyme-containing detergent granules of claim **16** wherein the nonionic surface active agent is selected from the group consisting of the condensation products of aliphatic, saturated or unsaturated, straight or branched chain, carboxylic acids having from about 10 to 18 carbon atoms with from 20 to about 50 moles of ethylene oxide; the condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohol having from about 10 to about 24 carbon atoms with from about 10 to about 50 moles of ethylene oxide; polyoxyethylene glyceride esters having a hydrophile-lipophile balance of about 18.1; polyoxyethylene lanolin derivatives having a hydrophile-lipophile balance of about 17.0; polyethylene glycols having a molecular weight of from about 1400 to about 30,000; the condensation products of one mole of alkyl phenol wherein the alkyl chain contains from about 8 to about 18 carbon atoms with from about 25 to about 50 moles of ethylene oxide; water-soluble amides having a melting point between 110° F. and 200° F.; fatty acids containing from about 12 to about 30 carbon atoms; fatty alcohols containing from about 16 to about 30 carbon atoms; glycerides selected from the group consisting of monoglycerides, diglycerides and mixtures thereof which melt between the temperatures of 110° F. and 200° F.

21. The enzyme-containing detergent granules of claim **16** wherein the nonionic surface active agent liquefies between the temperatures of from about 120° F. to about 150° F. and is selected from the group consisting of the condensation products of saturated or unsaturated, straight or branched chain acids having from about 10 to 18 carbon atoms with from about 20 to about 50 moles of ethylene oxide; and the condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohols having from about 10 to about 24 carbon atoms with from about 10 to about 50 moles of ethylene oxide.

22. A detergent composition having an active enzyme content of from about 0.005% to about 4.0% by weight of the detergent composition and having a nonionic content of from about 0.05% to about 15% by weight of the detergent composition comprising:

(1) from about 2% to about 30% by weight of the detergent composition of the finished granules of claim **16**, and

(2) from about 70% to about 98% of detergent granules containing builder salts and organic detergents in a weight ratio of from about 1:4 to about 30:1 and having a particle size distribution such that about 100% of the granules pass through a Tyler Standard 6 mesh screen and about 100% of the granules are retained on a Tyler Standard 200 mesh screen and having an average bulk density of from about 0.2 gm./cc. to about 0.8 gm./cc.

23. The detergent composition of claim **22** wherein the finished granules have an outside coating of from about 0.5% to about 5% by weight of the finished granules of a low-melting, ordinarily solid, water-soluble, nonionic surface active agent, which liquefies between the temperatures of from about 110° F. to about 200° F. and which is solid at temperatures below 110° F., said coating being applied over the enzymes conglutinated on said nonionic coating on said inner-core base granules.

24. The detergent composition of claim **22** having an enzyme composition content of from about 0.1% to about 2.0% of a proteolytic enzyme composition containing about 6% active enzyme derived from *Bacillus subtilis* and the remainder being essentially sodium sulfate and calcium sulfate.

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Dedication

3,519,570.—*Charles Bruce McCarty*, Cincinnati, Ohio. ENZYME-CONTAINING DETERGENT COMPOSITIONS AND A PROCESS FOR CONGLUTINATION OF ENZYMES AND DETERGENT COMPOSITIONS. Patent dated July 7, 1970. Dedication filed June 17, 1971, by the assignee, *The Procter & Gamble Company.*

Hereby dedicates to the Public the entire remaining term of said patent.

[*Official Gazette November 2, 1971.*]