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PROCESS FOR APPLICATION OF ENZYMES TO SPRAY-DRIED DETERGENT GRANULES

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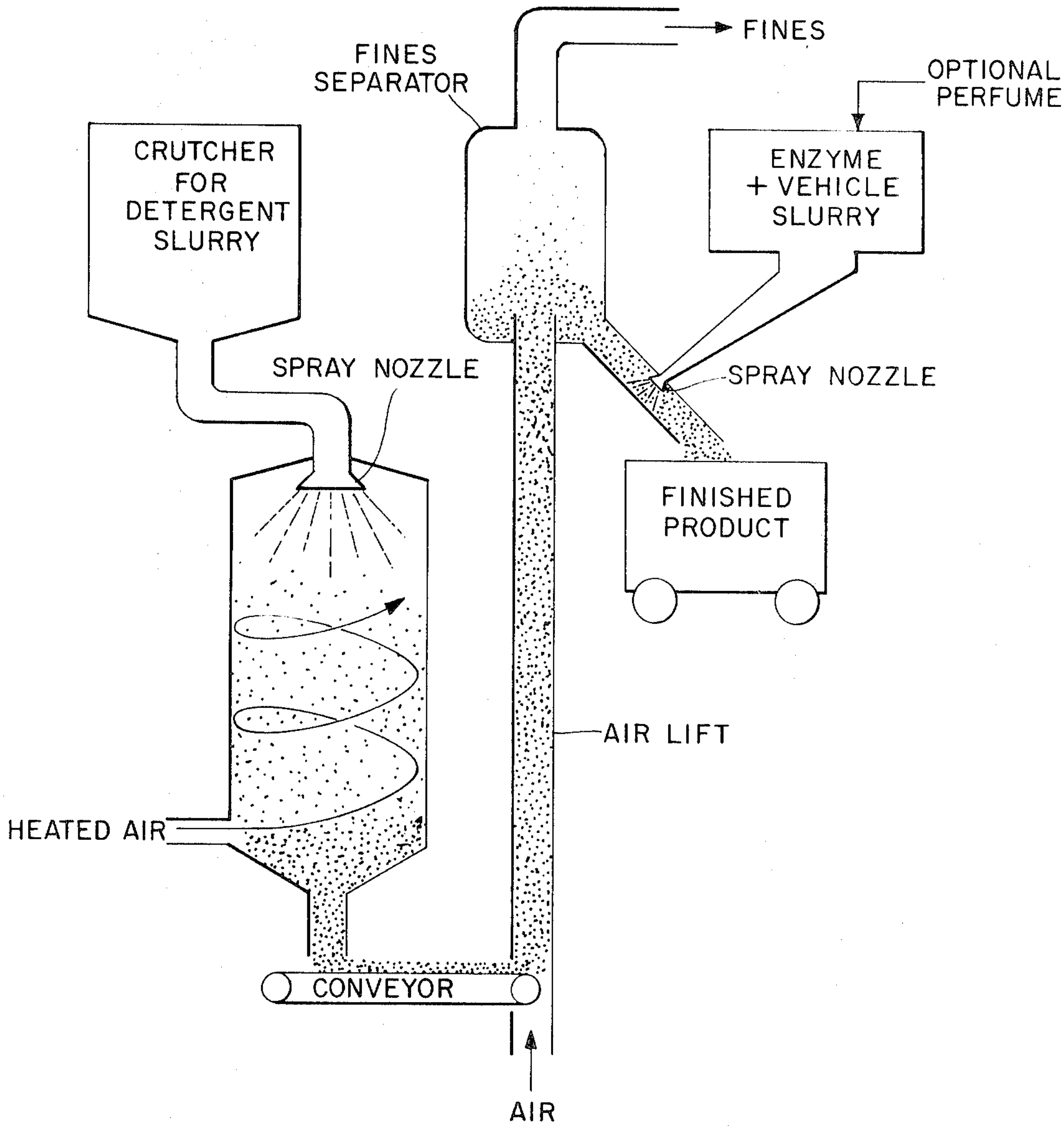

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PROCESS FOR APPLICATION OF ENZYMES TO SPRAY-DRIED DETERGENT GRANULES

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ABSTRACT OF THE DISCLOSURE

Enzymes are applied to spray-dried silicate-containing detergent granules by slurrying enzyme powder in a liquid, organic vehicle and spraying the slurry onto the granules at a temperature below 140° F.

This invention relates to a method for applying enzymes to laundry detergent granules from an organic liquid vehicle.

PRIOR ART AND BACKGROUND OF THE INVENTION

Laundry products containing enzymes are well known. 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 are usually used as a component of a laundry detergent formulation containing conventional cleaning ingredients, such as builders and organic detergents. 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, measure and formulate.

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

The prior art has taught some very good techniques for applying enzymes to detergent granules to overcome segregation and stability problems. For example, copending, commonly assigned application Ser. No. 630,199 of Roald and De Oude filed Apr. 12, 1967 teaches use of water to attach powdered enzymes to an hydratable granular carrier salt. Copending commonly assigned application of McCarty, Ser. No. 635, 293 filed Apr. 12, 1967, now Pat. No. 3,519,570, teaches the use of nonionic surface active materials to conglutinate powdered enzymes and detergent granules. These techniques, however, are not readily adaptable to the application of powdered enzymes to alkaline, silicate-containing, spray-dried detergent granules with the utilization of existing equipment.

Most granular detergent compositions are spray-dried from a hot, aqueous, alkaline, fluid slurry which contains sodium silicate. The manner of any enzyme addition to such compositions is critical, since the most useful enzymes for detergent compositions are very sensitive to alkalinity in the presence of moisture and to heat. These two environments must be avoided to the maximum possible extent. The problems presented by sodium silicate are especially significant since nearly all spray-dried laundry detergents contain an alkaline sodium silicate which is well known to be a corrosion inhibitor, a granules strengthening agent and a source of detergency-improving alkalinity. Detergent slurries are heated to elevated temperatures for spray drying generally in the range of 170° to 220° F. These heat and alkalinity-moisture factors make difficult effective incorporation of enzymes on silicate-containing spray-dried granules by any of the following means:

(1) addition to the hot fluid slurry prior to spray drying;
(2) addition to the tower or at the bottom thereof while the granules are warm and moist—temperatures within the spray tower usually range from about 600° F. at the air inlet to about 160° F. at the air exit;
(3) addition in the lower part of the airlift where the granules are cooled and dried (the granules are still too warm and the presence of unhydrated moisture would promote an attack on an enzyme by the silicate);
(4) addition, at the top of the air lift or in the fines separator after the granules have cooled, with a spray-on of a water-enzyme slurry (the use of an enzyme-water slurry would tend to expose the enzyme to an attack by the high alkalinity in the silicate-containing granules).

SUMMARY OF THE INVENTION

Notwithstanding the above problems, it was found that effective application of the enzyme to spray-dried, silicate-containing detergent granules, after they have been cooled to at least 140° F., preferably 120° F., can be effected by spraying powdered enzyme on to the granules in a slurry of a liquid organic vehicle. Such a vehicle provides a fluid enzyme slurry suitable for the usual spraying equipment. These liquid vehicles do not degrade the enzyme and they provide an application technique for attaching the enzyme to the spray-dried granules without exposing the enzyme to attack by silicate or other components of the granules. The liquid organic vehicle evaporates after application, leaving an enzyme-containing detergent granule having very good enzyme stability. The enzyme is applied and firmly attached to the granules in a way which is efficient, which can utilize existing equipment, which does not unduly expose the enzyme to the degrading effects of heat and moisture-supported alkalinity and which provides a stable non-segregating product. The application technique of the process of this invention is shown in the schematic drawing which is described in Example I.

DETAILED DESCRIPTION

The spray-dried granular detergent composition to which enzymes are applied by the process of this invention consists essentially of an organic detergent, an alkaline builder and sodium silicate. The organic detergent and alkaline builder range in weight ratio from about 2:1 to about 1:10, preferably 1:2 to 1:6. Together they comprise about 40% to about 97%, preferably 50% to 75%, of the spray-dried granules. These granules contain from about 3% to about 20%, preferably 5% to 10%, sodium silicate having a SiO_2:Na_2O ratio ranging from about 3.6:1 to about 1:1, preferably from 2.0:1 to 1.6:1. The granules have a pH in water solution of about 9 to 12, generally 9.5 to 11.5. The granules range in particle size from about .075 mm. to about 3.33 mm. (through 6 mesh and on 200 mesh-Tyler standard screens), preferably from 0.2 mm. to 2 mm. They range in density from about 0.2 gram/cc. to about 0.8 gram/cc.

At the time the enzyme slurry is sprayed on, the granules should have a free moisture content of less than 5% and preferably less than 2% in order to reduce attack on the enzyme by the silicate. Free moisture is moisture other than water of hydration in the granular components.

When the builder in the granules is sodium tripolyphosphate or other hydratable builder salt, free moisture often continues in the state of being taken up as water of hydration for a period after spray drying. This taking up continues even after the enzyme application, often to the point of 0% free moisture. Generally there is a reserve of hydration capacity, such that exposure of the granules to additional free moisture (from sources other than the initial detergent slurry which is spray-dried) does not result in undue attack on the enzyme by the alkalinity in the granule. Such additional free moisture is taken up as water of hydration and is therefore not readily available to stimulate an attack on the enzyme by the silicate alkalinity.

The organic detergent compounds used in the spray-dried granular detergent used in this invention are of the usual water-soluble anionic non-soap, nonionic, ampholytic and zwitterionic synthetic detergent classes or fatty acid soap. Of these, the anionic non-soap synthetic class, in the form of their alkali metal salts, are preferred. This class is usually characterized as organic sulfuric reaction products having in their molecular structure an alkyl radical containing from 8–22 carbon atoms and a sulfonic acid or sulfuric acid ester radical. This class is preferred because it is more readily spray dried than the other and has the best detergency characteristics. All of the above subclasses are described in additional detail in U.S. Pat. 3,351,558 issued to Roger E. Zimmerer Nov. 7, 1967, particularly from line 59, column 6 to line 74, column 9. This description is incorporated herein by reference.

The alkaline builders of the spray-dried detergent granules are of the usual classes, both inorganic and organic. The preferred classes of alkaline builder salts are the water-soluble alkali metal polyphosphates, aminopolyacetates, polyphosphonates and polycarboxylates. Representative examples of builder compounds of these classes are as follows: sodium tripolyphosphate, sodium pyrophosphate, sodium ethylenediaminetetraacetate, sodium nitrilotriacetate, sodium ethane hydroxy diphosphonate, sodium ethane-1-hydroxy-1,1,2-triphosphonate, and the polycarboxylates described in the patent of Francis L. Diehl, U.S. 3,308,067, issued Mar. 7, 1967. Other examples of suitable builders can be found in Zimmerer's U.S. Pat. 3,351,-558, especially from line 64, column 2 to line 38, column 3 which is incorporated herein by reference.

The spray-dried detergent granules can contain any of the other usual optional additives for such products including any of the following: inorganic fillers such as sodium sulfate in an amount up to about 35%; effective amounts of soil suspending agents such as sodium carboxymethyl cellulose, optical brighteners, dyes, germicidal agents, suds depressants, suds boosters, peroxy compounds, perfume and alkalinity agents such as NaOH, sodium carbonate or trisodium orthophosphate.

The enzymes attached to the spray-dried granules can be any of the catalytically active protein materials which are generally found in powdered form. Suitable enzymes degrade or alter one or more types or stains encountered in laundering situations so as to remove the soil or stain from the fabric being laundered or to make the soil or stain more removable by other detergent components. Both degradation and alteration improve soil removability.

The hydrolases, hydrases, oxidoreductases and desmolases degrade soil to remove it or make it more removable. The transferases and isomerases alter soil so as to make it more removable. Of these enzyme 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 protease having the broadest range of soil degradation capability.

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

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

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

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

The enzymes utilized in the process of this invention are generally obtained and stored in a dry, powdered form. The dry, powdered form is most easily handled and generally is more stable than enzymes in a water slurry. Enzymes per se have molecular diameters of from about 30 angstroms to several thousand angstroms. However, particle diameters of enzyme powder are normally much larger due to agglomeration of individual enzyme molecules or addition of inert vehicles such as organic clays, sodium or calcium sulfate or sodium chloride, during enzyme manufacture. Enzymes are grown in solution. Such vehicles are added after filtration of such solution to precipitate the enzyme in fine form which is then dried; calcium salts also stabilize enzymes. Enzyme powders used in this invention mostly are fine enough to pass through a Tyler Standard 20 mesh screen (0.85 mm.), although larger agglomerates are often found. Some particles of commercially available enzyme powders are fine enough to pass through a Tyler Standard 100 mesh screen. Generally a major amount of particles will remain on a 150 mesh screen. Thus, the powdered enzymes utilized herein usually range in size from about 1 mm. to 1 micron, and most generally from 0.1 mm. to 0.01 mm. The enzyme powders of the examples have a particle size in these ranges.

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, clay or starch as the remaining 98–20%. Specific active enzyme content of a commercial product is a result of manufacturing methods employed and is not critical herein so long as the resulting detergent granules have the desired enzymatic activity. Pure crystalline enzyme powder can also be employed. Many of the commercial enzyme products contain the preferred proteases as the active enzyme. In most cases, a subtilisin comprises the major portion of the proteases: other examples of hydrolases generally included in commercial products are lipases, carbohydrases, esterases and nucleases.

Specific examples of commercial enzyme products and the manufacture thereof include: Alcalase, Novo Industri, Maxatase, Koninklijke Nederlandsche Gist En Spiritusfabriek N.V., Protease B–4000 and Protease AP, Schweizerische Ferment A.G., CRD-Protease, Monsanto Company, Viokase, Viobin Corporation, Pronase–P, Pronase–AS and Pronase–AF, Koken Chemical Company, Japan; Rapidase P–2000, Rapidase, France; Takamine, Bromelain 1:10, HT proteolytic enzyme 200, Enzyme L–W (derived from fungi rather than bacteria), Miles Chemical Company, Rhozym P–11 concentrate, Pectinol, Lipase B, Rhozyme PF, Rhozyme J–25, Rohm and Haas, Rhozyme PF and J–35 have salt and corn starch vehicles and are proteases having diastase activity; Amprozyme 200, Jacques Wolf & Company.

An enzyme product preferred for use in the detergent compositions of this invention is a proteolytic enzyme, a serine protease, with the trade name of Alcalase, Alcalase has been described as a proteolytic enzyme preparation manufactured by submerged fermentation of a special strain of *Bacillus subtilis.* The primary enzyme component of Alcalase is subtilisin. Alcalase is a fine grayish powder having a crystalline active enzyme content of about 6% and a particle size ranging from 1.2 mm. to .01 mm. and smaller, about 75% passing through a 100 mesh Tyler screen. The remainder of the powder is comprised primarily of sodium chloride, calcium sulfate and various inert organic vehicle materials.

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 used for streptomycin manufacture. They are isolated by the successive resin column treatment. The major component of the Pronases is a neutral Streptomyces griseus protease. This enzyme product contains a calcium stabilizer salt.

CRD–Protease is reported to be obtained by mutation of a *Bacillus subtilis* organism. Its proteolytic content is about 80% neutral protease and 20% alkaline protease. It contains some amylase. 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 from 0.03 mm. to 0.1 mm.

The particular enzyme chosen for use in the process of this invention depends on the composition pH, use pH, use temperature and soil types to be degraded or altered. The enzyme can be chosen to provide optimum activity and/or stability for any given set of utility conditions. Enzymes active in the pH range of 7–11 are used. Most readily available and suitable are those active in the 8–10 pH range.

The powdered enzymes are attached to the spray-dried granular detergent in the process of this invention to provide an active enzyme content ranging from about 0.001% to 2%, generally 0.005% to 0.5% of the spray-dried detergent granules. Taking into account inert vehicles in commercial powdered enzyme products, the amount of enzyme products (enzyme+vehicle) attached to the granular carrier can range up to 20%, of the weight of spray-dried granules.

The organic liquid vehicle with which the powdered enzyme is slurried is an organic, low-boiling solvent which is pure enough to leave no undesirable residue upon evaporation. The solvent should have a boiling point within the range of about 55° to about 110° C. so as to be liquid and easily handled at ambient temperatures (65° F.–100° F.) or below and to evaporate readily after application to the granules. Any of the many well-known organic liquids having the above characteristics are suitable for use in the process of this invention. Such liquids should have evaporation rates no faster than that of acetone and no slower than that of isopropanol (rates ranging from 110 to 1160). See the tables in the Kirk Othmer Encyclopedia of Chemical Technology, volume 12, pp. 666–7 et seq. (1954), incorporated herein by reference. Specific examples of such suitable solvents are: lower monohydric alcohols such as methanol, ethanol, propanol, isopropanol and isobutanol; lower ketones such as acetone and methyl ethyl ketones; lower alkane hydrocarbons such as hexane and heptane; halogenated alkanes such as ethylene dichloride; aromatic hydrocarbons such as benzene and toluene. Organic liquids such as ether, Freons, and petane are too volatile. Organic liquids such as phenol, cyclohexanol, octane, butanol, dimethyl sulfoxide and dimethyl formamide, have boiling points which are too high. The suitable organic liquids can tolerate up to 10%, preferably no more than 5%, water without losing their non-aqueous characteristics and their suitability for use herein. Preferably they are used in an anhydrous state. The slurry of enzyme plus organic liquid should be prepared and used at ambient temperatures or below (e.g. in the range of 40°–100° F.) in order to avoid any tendency to denature the enzyme. The solubility of enzymes in the organic liquids suitable for use in the process of this invention is quite low. The powdered diluents with which the enzymes are associated also have a low solubility in the organic liquid.

These vehicles are relatively safe to handle; they are fluid; they are non-reactive with the enzyme, they are easily sprayed and evaporate readily, resulting in firm even attachment of the enzyme to the spray-dried granules. Moreover, they are suitable vehicles for perfume if it is desired to add enzyme along with an effective amount of perfume to the finished spray-dried granules in the same spray-on step. Perfume must be added to spray-dried granules after they are relatively cool because perfume would be degraded and/or wasted by application to hot granules. Ethanol is preferred because it is easily handled and evaporates readily.

While it is desired not to be bound by theory it is believed that the organic liquid vehicle employed to slurry the enzyme and sprayed on to the spray-dried granules softens or dissolves a small amount of the organic detergent compound in the granules. This softened or dissolved detergent compound then associated with the enzyme, at least partially encapsulating it after the organic liquid evaporates. Such encapsulation help protect the enzyme and also provides a stronger adherence of the enzyme to the spray-dried granule.

In practicing the process of this invention the powdered enzyme or enzyme product (enzyme plus powdered vehicle) is slurried uniformly with the organic liquid vehicle, preferably at ambient temperatures. The proportion of vehicle to enzyme should be at least about 1:1 and can range up to 15, preferably 10, parts liquid vehicle to each part enzyme powder. Sufficient vehicle should be used to make the slurry fluid, pumpable and sprayable. Organic liquid vehicle substantially in excess of the amount needed to make a fluid slurry is wasteful and creates problems in handling the vapors resulting from evaporation thereof.

The slurry of enzyme powder and organic liquid vehicle is sprayed on to the spray-dried granules while the granules are in an agitated dispersed state, preferably flowing in a moving stream of air. A preferred point of application is at or near the top of the usual air lift, beside a spray tower, in which the spray-dried granules are cooled and dried. Often at the top of this air lift is a fines separator which is an especially convenient place to spray on the slurry of enzyme and organic liquid vehicle. Other methods of spray-on can be employed so long as the above described conditions are observed and can include the following: granules can be conveyed and cooled from the bottom of the tower, e.g., on a conveyor belt, and then introduced into a tumble drum where the spray-on of enzyme+vehicle can be affected. After the spray-on by any means, the organic vehicle readily evaporates into the atmosphere. Special attention to such evaporation is not necessary, although venting fans for finished product bins or other containers are desirable.

The process of this invention is illustrated with the examples which follow. The process is that illustrated in the drawing which shows schematically the apparatus arrangement employed. Examples are not to be regarded as limiting the invention. All amounts and percentages and ratios in the specification, examples and claims are by weight unless otherwise indicated.

EXAMPLE I

Spray dried detergent granules are prepared in a spray tower by slurrying the following detergent ingredients in a crutcher at 180° F. with sufficient water (about 40%) to make a pumpable sprayable slurry then spray drying the slurry through nozzles in the spray tower. The tower contains countercurrent flowing air heated to 600° F. at the inlets and exiting from the tower at 190° F. The granules are spray dried to the composition as shown below having an average particle size of about 0.5 mm. and a bulk density of about 0.3 gm./cc.

	Percent
Anionic organic synthetic detergent consisting of sodium linear dodecyl benzene sulfonate and sodium tallow alkyl sulfate in 55:45 ratio	17.3
Monoethanolamide of coconut fatty acid	2.3
Sodium tripolyphosphate	50
Sodium silicate (SiO_2:Na_2O ratio of 1.6:1)	6
Sodium carboxymethyl cellulose	0.3
Sodium sulfate	13.9
Perfume	0.13
Water	10
Brighteners	.07

The 10% water in the granules is mostly in the form of water of hydration in the sodium tripolyphosphate; the free moisture in the granules is about 2% in the exit tube of the fines separator at the top of the air lift. The granules temperature in the exit tube is about 120° F. At the exit tube of the fines separator, a slurry of enzyme powder in ethanol is uniformly sprayed on to the spray dried granules which are flowing in an agitated dispersed state. The spray is directed into the exit tube using a pumping pressure of 80 p.s.i. and a standard spray nozzle. The enzyme powder in the slurry is Alcalase (defined above). This slurry is at room temperature and comprises one part Alcalase and 9 parts ethanol. The ethanol is denatured with 5% methanol. Sufficient enzyme slurry is sprayed on to the spray dried granules to provide an Alcalase content of 0.10% content by weight of the detergent composition. The alcohol vehicle evaporates quickly from the granules which are sent to finished product storage.

The pH in water solution of the spray-dried granules is 9.7. The enzyme powder is firmly attached to the granules. The resulting detergent composition has no segregation disadvantages and retains its enzyme activity for prolonged storage periods. It is an effective laundry detergent with the enzyme content providing significant extra cleaning and soil degrading and soil and stain removal capabilities.

The process of this example is repeated to achieve an Alcalase content of 0.05% in the granular detergent, instead of 0.10%, with substantially equivalent results except with a lower level of enzymatic activity.

EXAMPLE II

The process of Example I is repeated again except that the alcohol-Alcalase slurry had a weight ratio of 3 parts ethanol to 1 part Alcalase. The enzyme-alcohol slurry is applied at three different levels: one to provide 1% Alcalase in the treated spray-dried granules, another level to provide 0.1% and another level to provide 0.05%. These treated spray-dried detergent granules, with firmly attached enzyme, are also highly stable and effective laundering agents. They retain their enzymatic activity over prolonged storage periods including storage at higher temperatures.

The process of Example II is repeated except that the spray-dried granules initially were perfume-free. The perfume intended for the granules is admixed with the enzyme-ethanol slurry so as to provide a perfume level in the treated spray-dried granules of 0.11%. This enzyme perfume application and the resulting spray-dried granules are quite satisfactory in all respects.

Substantially equivalent results can be obtained in the above examples employing any of the many powdered enzymes having soil removal or soil and stain degradation capabilities. Likewise substantially similar results can be obtained by using other organic liquid vehicles instead of ethanol, such as methanol, propanol, isopropanol, benzene, hexane or acetone.

Substantially similar results can also be obtained by using different formulations for the spray-dried granules. Other organic detergents can be used such as: sodium coconut oil soap, the condensation product of 1 mole of coconut fatty alcohol and 6 moles of ethylene oxide; 3 - (N,N, - dimethyl - N - dodecylammonio) - 2 - hydroxypropane-1-sulfonate. Other builders can be used in place of the sodium tripolyphosphate, such as tetrasodium pyrophosphate, trisodium nitrilotriacetate, trisodium ethane - 1 - hydroxy - 1,1 - diphosphonate or mixtures of any of these. Mixtures of sodium tripolyphosphate and trisodium nitrilotriacetate are very good.

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

What is claimed is:

1. A process for applying enzymes to spray-dried detergent granules which consist essentially of an organic detergent selected from the group consisting of water-soluble anionic non-soap synthetic detergents, water-soluble non-ionic non-soap synthetic detergents, water-soluble ampholytic non-soap synthetic detergents, water-soluble zwitterionic non-soap synthetic detergents, and fatty acid soaps, an alkaline builder selected from the group consisting of water-soluble inorganic alkaline builder salts, organic alkaline sequestering builder salts, and mixtures thereof, and sodium silicate comprising the steps of preparing a fluid slurry of enzyme in a liquid, organic vehicle having a boiling point in the range of about 55° C. to about 110° C., an evaporation rate in the range of about 110 to about 1160, and selected from the group consisting of lower monohydric alcohols, lower ketones, lower alkane hydrocarbons, halogenated alkanes, and aromatic hydrocarbons, and spraying said slurry onto said granules which are at a temperature of less than about 140° F. and have less than 5% free moisture.

2. The process of claim **1** wherein the organic detergent is selected from the group consisting of sulfate anionic non-soap synthetic detergents and sulfonate anionic non-soap synthetic detergents, the ratio of detergent to buider ranges from about 2:1 to about 1:10 and the silicate content is from about 3% to 20%, and the organic vehicle is selected from the group consisting of methanol, ethanol, propanol, isopropanol, isobutanol, acetone, methyl ethyl ketones, hexane, heptane, ethylene dichloride, benzene, and toluene.

3. The process of claim **2** wherein the vehicle is ethanol, the enzyme consists essentially of protease, the ratio of vehicle to enzyme is at least about 1:1 and the temperature is less than 120° F., and the said ratio ranges from 1:2 to 1:6.

4. The process of claim **3** wherein the silicate in the granules is from 5% to 10% and has an SiO_2:Na_2O ratio of from 2.0:1 to 1.6:1, the detergent and builder together are from 50% to 75% of the granules, the free moisture content of the granules is less than 2% and the enzyme content of the product of the process is from about .001% to about 2%.

5. The process of claim **4** wherein perfume is included in the said slurry.

6. The product of the process of claim **4**.

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Dedication

3,600,319.—*Burton H. Gedge III*, Wyoming, and *Charles H. Brain*, Mount Healthy, Ohio. PROCESS FOR APPLICATION OF ENZYMES TO SPRAY-DRIED DETERGENT GRANULES. Patent dated Aug. 17, 1971. Dedication filed Nov. 5, 1971 by the assignee, *The Procter & Gamble Company*.

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

[*Official Gazette February 29, 1972.*]