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3,749,671

PROCESS OF PRODUCING ENZYME COMPOSITIONS

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No Drawing. Filed July 1, 1971, Ser. No. 159,032
Int. Cl. C11d 7/42

U.S. Cl. 252—89

12 Claims

ABSTRACT OF THE DISCLOSURE

Prills comprising an enzyme and a normally solid water-soluble translucent material are made by a process wherein the resultant prills have a relatively light color. A slurry of the enzyme and normally solid water-soluble translucent material is injected with an inert gas and then made into prills by any prilling method. An especially preferred method of making the prills is by spray cooling. The inert gas injection step prior to prilling results in prills having a Hunter color L-value of about L-70 to L-90, significantly higher than the L-value of prills made by a prilling technique not employing the inert gas injection step. Each of the resultant prills is in the form of a substantially spherical shape having a substantially smooth outer surface and porous interior.

BACKGROUND OF THE INVENTION

This invention relates to a process of producing prills comprising an enzyme and a normally solid water-soluble material. The prills have particular utility as a component of a washing composition.

Enzymes are well known and have been used as cleaning aids for many years. Enzymes are used either in a 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 produced in a powdered form. Because enzymes are in such a form, they are hard to handle, difficult to measure, and, as some reports have indicated, may represent a hygiene concern.

In addition to the above disadvantages of powdered enzymes, there are other drawbacks associated with powdered enzymes in a granular laundry product. For instance, powdered enzymes have a tendency to segregate from the laundry product's other components. The incompatibility of the enzymes with other components normally included in a laundry product and moisture is another problem associated with enzyme-containing detergents. For these reasons, some prior art laundry products have attempted to alleviate or eliminate the foregoing problems by encapsulating the enzymes with a compatible material. By so doing, the enzyme is less exposed to moisture and other components of the laundry composition, and is less likely to cause a hygiene concern. The reason for the latter advantage is that the encapsulation material insulates the enzyme and diminishes the amount of enzyme that is free as "dust." However, a drawback encountered with such encapsulated enzymes has been the unacceptable dark color associated with such materials. Generally, the enzyme is a dull, dark colored substance and the encapsulating material is of a translucent nature so that the encapsulating enzyme material is of the same dull dark color as the enzyme itself. While this fact may not affect the performance of the detergent composition containing the encapsulated enzyme, it does create an unfavorable impression in the average housewife. Accordingly, some prior art encapsulated enzymes have included within

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them an inert coloring material, e.g. titanium dioxide to improve their appearance. Certain limitations, though, such as the discovery of the proper inert coloring material and an extra material handling step have hampered the use of colorants as a solution to the dull, dark, unattractive color of the encapsulated enzymes.

Accordingly, it is an object of this invention to produce enzyme-containing materials that have a pleasing appearance.

More specifically, it is an object of this invention to produce an enzyme-containing prill having a pleasing appearance by a novel process.

It is still another object of this invention to produce an enzyme-containing prill having a pleasing color that is attributable to the prill's physical structure.

These and other objects will become apparent from the description that follows.

SUMMARY OF THE INVENTION

Enzyme-containing prills possessing a pleasingly light color are produced by a process comprising the steps of (a) heating a normally solid water-soluble translucent material to a temperature sufficient to melt the material but insufficient to destroy the activity of an enzyme; (b) mixing with the melted material an enzyme to form a slurry having dispersed therewithin from 5% to 50% of the enzyme by total weight; (c) injecting an inert gas into the slurry to form therewithin a uniform dispersion of said gas; and (d) forming prills from the slurry of step (c). The resultant prills are much lighter in color than prills made by the same process without the inert gas injection step and accordingly have a more pleasing appearance. The pleasingly light color of the prills is attributed to their unique physical structure wherein each prill is in the form of a substantially spherical shape having a substantially smooth surface and a porous interior. Prills made by this process are capable of being mixed with granular cleaning compositions to yield free-flowing products with good stability and color.

DESCRIPTION OF THE INVENTION

The process of this invention produces a light colored prill comprising an enzyme and a normally solid water-soluble translucent material.

The enzymes useful in this invention are any of the enzymes commonly used in detergent compositions. Specifically, the enzymes useful in this invention are described in U.S. Pat. No. 3,519,570 (herein incorporated by reference). The enzymes suitable for use are those that are active in a pH range from 4 to 12 and preferably are active in the pH range of from 7 to 11 and at a temperature in the range of from 50° F. to 185° F., preferably from 70° F. to 170° F.

The enzymes commercially available are generally dry powdered products comprised of from about 2% to 80% active enzymes in combination with an inert powdered vehicle such as sodium or calcium sulfate, sodium chloride, clay, or starch as the remaining 98%—20%. As used herein, the term "enzyme" refers to the aforementioned enzyme products, i.e. the products containing about 2% to 80% active enzyme.

In preferred forms of this invention, the enzyme comprises a proteolytic enzyme, amylase enzyme, or mixture thereof. Examples of proteolytic enzymes that can be used in the present invention include pepsin, trypsin, chymotrypsin, papain, and bromelain. Particularly preferred enzymes are the subtilisins manufactured and cultured from special cultures of spore forming bacteria, e.g. *Bacillus subtilis*. A bacterial amylase of the alpha type is

an example of an amylase enzyme that can be present either alone or in combination with a proteolytic enzyme in the present invention.

The prills produced by this invention have included therewith in addition to the above-mentioned enzymes a normally solid water-soluble translucent material. More specifically, the normally solid water-soluble translucent materials of this invention melt or liquefy between the temperature of 110° F. and 200° F., preferably between 120° F. and 150° F. A wide variety of materials fitting the above criteria and compatible with the enzymes of this invention are useful in the context of the present invention. Particularly preferred are the nonionic materials.

Specific examples of materials suitable for use in 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 atoms 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% C₁₀, 66% C₁₂, 23% C₁₄ and 9% C₁₆ 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% C₁₀, 66% C₁₂, 23% C₁₄ and 9% C₁₆ with 45 moles of ethylene oxide (CNAE₄₅) 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 hydrophilic-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) Amides which have a melting point between about 10° F. and 200° F. 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 car-

bon 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 a carbon chain lengths of from about 6 to about 10 carbon atoms, N-cyclopentyl lauramide and N-cyclopentyl stearamide.

(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 acid 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 ligoceric acid. Fatty acids are nonionic when utilized as a 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.

Normally solid water-soluble materials other than those listed above can also be used in this invention provided they are compatible with the enzyme and are of a translucent nature.

According to this invention, the enzyme and normally solid water-soluble translucent material are made into a slurry by heating the normally solid material to a temperature sufficient to melt it and mixing therewithin the enzyme material. With regard to the temperature of the melted material, care must be exercised that the activity of the enzyme is not destroyed thereby. Accordingly temperatures greater than about 200° F. are avoided. The enzyme concentration of the slurry and prills made therefrom vary over a wide range. A range of from 5% to 50% on a total weight basis of enzyme dispersed within the slurry has been found to be suitable for this invention. Preferably from 7% to 20% of enzyme based on the total weight of the slurry is used in this invention.

After the enzyme and melted material are thoroughly mixed, an inert gas is injected into the slurry. Examples of inert gases (inert, that is, to the enzyme and normally solid water-soluble material) are nitrogen, carbon dioxide, and air. Gases useful in this invention are not limited to the above three, it being understood that any gas that is inert is used. The amount of gas that is injected into the slurry is dependent on the degree of color change desired in the final product of this process, i.e. the prill. To an extent, the greater the amount of inert gas injected into the slurry, the greater will be the change in color. The limiting factor as to the upper range of amount of inert gas injection is the ability of the slurry to dissolve or have uniformly dispersed therewithin the inert gas. That is, a point is reached, at which further injection of inert gas will cause the formation of pockets of gas within the slurry which in turn will hamper the operation of the

process. The exact amount of inert gas that is effectively injected into the slurry in order to get a desired color change will vary depending on the particular normally solid water-soluble material being employed and the temperature of the slurry prior to injection of the said inert gas. The quantitative amount of inert gas injected into any one particular slurry is determined by experimentation based on the disclosure set out herein.

As used herein the color of the prills is measured in numerical terms by the use of a Hunterlab Model D25 Color and Color Difference Meter. Such a meter is made by Hunter Associates Laboratory, Inc. of Virginia. The color is expressed in Hunter L-values, whereby the least significant difference at 95% confidence level is 1 L. The higher the L-value, the more light or white is the sample being measured.

Enzyme-containing prills made by the prior art processes of no inert gas injection and with no coloring matter added thereto typically have a Hunter color L-value ranging from L-40 to L-65. Preferably an amount of inert gas is injected into the slurries of this invention to give the subsequently produced prills as described below a Hunter color L-value ranging from L-70 to L-90. Such an increase in the L-values represents a change from a dull brownish color to a whitish color. Most preferably the prills of this invention have a Hunter color L-value of from L-80 to L-90.

Accompanying the color change is a reduction in the density of the prills. Depending on the degree of color change desired, the density of the prills of this invention can be reduced by as much as 60%. The greater the degree of color change desired, as measured by the Hunter color scale L-value, the greater will be the reduction in density.

The slurry after the inert gas injection step is next manipulated to form small solidified beads, or as more commonly referred to, prills. These solidified prills are substantially spherical-shaped and free flowing. More particularly, the solidified prills of this invention have a substantially smooth outer surface and a porous interior. By a substantially smooth surface is meant that the surface is fairly even, i.e. not rough or broken. By a porous interior is meant that the interior is composed of a homogeneous mixture of solidified enzyme and translucent material having substantially uniformly distributed there-through a mass of voids such that a cross-section of the interior resembles a substantially pockmarked substrate.

A particularly preferred method of forming the prills of this invention is to spray the inert gas-injected slurry into a fresh atmosphere. The spraying in effect forms small droplets that, after cooling, solidify into prills. In a typical spray cooling operation the slurry is sprayed into the top of a tower, the height of which can vary considerably. At the base of the tower, a source of cool air, i.e. air having a temperature of from 40° F. to 60° F., is introduced. As the falling spray droplets are contacted by the rising cool air, the normally solid material solidifies to form the prills. The resultant prills are collected at the base of the tower and the cool air exits at the top of the tower.

The prill particle size can be controlled by regulating the size of the spray drops of the slurry. In turn, the size of the spray drops will depend on factors such as the viscosity of the slurry sprayed, the spraying pressure and the nature of the spraying head, e.g. the outlet orifice size. Generally, the particle diameter of the prills of this invention is below about 1 mm. The above parameters are determined by routine experimentation. Based on the temperatures of the slurries above disclosed it has been found that spray pressures ranging from 110 p.s.i. to 2,000 p.s.i. and a spray outlet orifice of from 0.040 inch to 0.125 inch produces prills of the desired size.

Surprisingly, the resultant prills of this invention are very light in color. The reason for the pleasingly light color is attributable to the physical structure of the prills.

The outer portion of the prill is substantially smooth. However, examination of the dissected prills under a microscope indicates that the inert gas has been dispersed in the slurry and upon release of pressure at the spray nozzle has produced a mass of very fine voids or bubbles uniformly distributed in the interior of the prills. It is theorized that the fine dispersion of voids in the prills causes light to be broken up and reflected in such a manner that an improvement in color results, i.e. the color of the prills is significantly lighter in color than prills produced by a method that does not have a gas injection step. Thus can be seen the importance of the normally solid material being translucent. As such, the novel structure of the prills of this invention causes the reflection of light in such a manner that it is the structure itself that is responsible for the color of the prill. An opaque material in combination with an enzyme and having the structure above referred to would not possess the same color as the product of this invention.

The enzyme-containing prills of this invention are added to a wide variety of washing formulations. For instance, they are incorporated into a presoak laundry product, a laundry detergent, or an automatic dishwashing product. Usually the proportion of enzyme-containing prills in such cleaning products is in the range of from 0.5% to 5% by weight.

While the above description has had particular reference to the production of enzyme-containing prills, the process of this invention can be used for the making of prills containing many other materials whenever a change in color is desired.

The following examples are given to illustrate the novel process of this invention. All percentages are on a dry weight basis.

Example I

418 pounds of a nonionic translucent material identified as "Wyandotte 7135 Encapsulating Agent" was heated to a temperature of about 150° F. in an agitated container to completely melt it. The above material was supplied by the Wyandotte Chemical Corp. and was described as a mixed polyethylene glycol-polypropylene glycol material. To this melt was added 32 pounds of an enzyme preparation having protease and amylase activity to form a slurry containing 7.1% enzyme by weight. The slurry was next pumped to a spray nozzle of a spray-cooling tower. The tower was about 50 feet in height and 10 feet in diameter. The spray nozzle had an orifice of 0.067 inch and was located at the top of the tower. Cool air of about 48° F. was introduced at the bottom of the tower and exited at the top. Nitrogen gas under a pressure of 1,000 p.s.i.g. was injected into the slurry as it flowed through a pipeline from the agitated slurry tank to the spray nozzle. Pressure at the spray nozzle head was 400 p.s.i.g. The resultant prills had a density of about 20.5 oz./100 cu. in. The Hunter color as measured on the L-scale of a Hunter Color and Color Difference Meter, model D25, was L-79.8. This corresponds to a white color.

The enzyme containing prills prepared by this example are useful in detergent compositions. Enzymatic activity is retained and imparted to detergent compositions containing them.

For comparison purposes, the same procedure as above was run with the exception that no gas was injected into the slurry and the spray nozzle pressure was 300 p.s.i.g. The use of this slightly lower nozzle pressure had no measurable effects on the color of the resultant prills. The resultant prills had a density of 37 oz./100 cu. in. and a color value of L-63.2. This L-value represents a brown color.

The following examples are of slurry compositions that when injected with gas in the manner described in Example I above produce prills having light colors within the L-70 to L-90 range. The prills are substantially lighter in color than prills produced from the slurries with-

out the employment of the gas injection step. Enzymatic activity is retained and the resulting prills are useful in detergent compositions.

Example II

	Lbs.	
Carbowax 6000 of average molecular weight 6000-7500 (heated to a temperature of 150° F. to cause melting) -----	95	
Protease TP (active protease content of about 9%) --	5	10

Example III

	Lbs.	
Condensation product of one mole of coconut alcohol and 45 moles of ethylene oxide (heated to 135° F. to cause melting) -----	50	
Milezyme (active enzyme content of 5% alkaline protease and 6% amylase activity) -----	50	

Results substantially similar to those achieved in the previous examples are obtained when other ordinarily solid, water-soluble materials melting between the temperatures of 110° F. and 200° F. are substituted for the materials hereinbefore utilized in that the resulting product has a color substantially lighter, i.e., Hunter color L-70 to L-90 than a product made by a different process. When in the above examples, the following materials are substituted, either wholly or in part for the above exemplified normally-solid materials, substantially similar results are obtained: the condensation product of one mole of coconut fatty acid having the approximate chain length distribution of 2% C₁₀, 66% C₁₂, 23% C₁₄ and 9% C₁₆ 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 mol 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 and 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-cyclopentyl lauramide and N-cyclopentyl stearamide.

What is claimed is:

1. A process of producing enzyme-containing prills characterized in having a pleasingly light color attributable to the physical structure of the prills, each of said prills being in the form of a substantially spherical shape having a substantially smooth outer surface and a porous interior, consisting essentially of:

- heating a normally solid water-soluble nonionic translucent material to a temperature sufficient to melt the material but insufficient to destroy the activity of an enzyme;
- mixing with the melted material an enzyme to form a slurry having dispersed there-within from 5% to 50% enzyme by total weight;
- injecting an inert gas into the slurry to form there-within a uniform dispersion of said gas; and
- forming prills from the slurry of step (c) having said physical structure and color.

2. The process claim 1 wherein an inert gas is injected into the slurry in an amount sufficient to produce enzyme-containing prills having a Hunter color L-value ranging from L-70 to L-90.

3. The process of claim 2 wherein the prills are formed by spray cooling the slurry of step (c).

4. The process of claim 3 wherein the normally solid water-soluble material has a melting point ranging from 110° F. to 200° F.

5. The process of claim 4 wherein the inert gas is selected from the group consisting of nitrogen, carbon dioxide, and air.

6. The process of claim 5 wherein the normally solid water-soluble nonionic translucent material is polyethylene glycol having a molecular weight of from 1,400 to 30,000.

7. The process of claim 6 wherein the Hunter color L-value is from L-80 to L-90.

8. The process of claim 7 wherein the Hunter color L-value of the enzyme prior to mixing with the melted material is from L-40 to L-65.

9. A substantially spherical-shaped prill consisting essentially of from 5-50% of an enzyme and a normally solid water-soluble nonionic translucent material characterized in having a pleasingly light color attributable to its physical structure, said prill having a substantially smooth outer surface and a porous interior.

10. The prill of claim 9 wherein the Hunter color L-value ranges from L-70 to L-90.

11. The prill of claim 9 wherein the nonionic material is polyethylene glycol having a molecular weight of from 1,400 to 30,000.

12. The prill of claim 10 wherein the interior is composed of a homogeneous mixture of the enzyme and translucent material having substantially uniformly distributed therethrough a mass of voids.

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U.S. Cl. X.R.

195-63, 68; 252-DIG. 12