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[54] **DETERGENT COMPOSITION CONTAINING ENZYMES**

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[51] **Int. Cl.**..... **C11d 7/38**

[58] **Field of Search**..... 252/99, 89, DIG. 12; 195/63, 68, DIG. 11

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[57] **ABSTRACT**

A granular detergent composition containing (a) an organic detergent, (b) an alkaline builder, (c) glucose polymers with an α-1,4 main linkage, (d) a compound of the general formula R_1 —$(CHOH)_n$—Y, wherein Y represents a salt or an ester radical derived from a carboxylic radical, n is 3 or 4, and R_1 is CH_2OH or CHO, and (e) an α-amylase. The glucose polymers and the compound of the general formula $R_1(CHOH)_n$—Y protects the α-amylase against denaturation and degradation.

14 Claims, No Drawings

DETERGENT COMPOSITION CONTAINING ENZYMES

This invention pertains to granular detergent compositions containing α-amylase; this latter ingredient is protected against denaturation and degradation through the use of a protective system comprising glucose polymers with an α-1,4 main linkage in admixture with derivatives of monosaccharides as hereinafter more fully explained.

Amylolytic activity is related to the amylase structure which is highly sensitive to several factors which are of major importance during storage. The rate of decrease in amylolytic activity is especially high when the granular detergent compositions contain peroxy bleach compounds and the enzyme species are exposed to temperatures at or above ambient temperature and/or to a high relative humidity. Work has already been undertaken to overcome the amylolytic stability difficulties which are encountered in detergent compositions particularly during prolonged storage. The teachings of Danish patent specification 64.721 suggest that diastases (i.e., vegatable amylases) can satisfactorily be protected in granular detergent compositions by the use of a protective coating consisting of a protinaceous substance such as gelatin. It is also mentioned that starch and the like ingredients are to be avoided for the stabilization of diastatic enzymes. From Swiss patent specification No. 282,704, it can be deduced that the enzymatic activity retention of desizing compositions is very critical, particularly when the storage takes place in an humid atmosphere. The addition of calcium sulfate in form of gypsum is suggested as a remedy for the deficient amylolytic stability during storage.

It has now been found that an unexpected amylolytic stability retention during prolonged storage is attainable in granular detergent compositions containing surface-active agents, builders, enzymes and other usual detergent ingredients comprising;

a. an organic detergent,

b. an alkaline builder selected from the group consisting of an organic sequestering builder, an inorganic alkaline builder and mixtures thereof, the proportion of said detergent to said builders being in the range of from about 10:1 to 1:30;

c. glucose polymers with an alpha-1,4 main linkage in a weight ratio of said ingredient to pure alpha-amylase of 1:1 to 5,000:1;

d. a compound of the formula $R_1 - (CHOH)_{3 \text{ or } 4} - Y$ wherein Y represents a salt- or an ester-radical derived from a carboxylic radical, R_1 is CH_2OH, or CHO and whereby the weight ratio of this compound to said glucose polymers is from 2:1 to 1:100; and

e. from 0.0005 percent to about 3 percent of alpha-amylase calculated on the basis of pure alpha-amylase.

Alpha-amylases are well known enzymes. They are particularly well suited for use in granular detergent compositions because they break down starch molecules by attacking the alpha-1,4-glucosidic linkages in starchy soils and stains. The resultant shorter molecular chains in these soils and stains are then more readily removed by water or aqueous solutions of detergents. The alpha-amylases can be obtained from animal, fungal, cereal grain and bacterial sources. Alpha-amylases of this latter source are preferred because of their ready availability, high activity, a degree of inherent resistance to detergent inactivation and ready stabilization against inactivation in granular detergent compositions in the presence of a stabilizing mixture comprising glucose polymers and derivatives of monosaccharides.

Numerous methods have been described for the determination of alpha-amylase activity. A modification of the saccharifying activity assay developed by P. Bernfeld : *Adv. in Enzymology* 12, 385 (1951) can be used in the determination of the activity of the alpha-amylases used in compositions of this invention. In this method, a sample of alpha-amylase is permitted to catalyze the hydrolysis of the alpha-1,4 glucosidic bonds of starch for 5 minutes at a pH of 6.0 and a temperature of 37° C. The reaction is stopped by the addition of an alkaline solution of 3,5-dinitrosalicylic acid and Rochelle salt. The brown colour of the reaction products which is developed in the analytical sample is compared spectrophotometrically with that developed by standard solutions of maltose hydrate. One amylase activity unit is assigned for each 0.4 mg. of maltose hydrate produced during hydrolysis. In practice, it is found that the amount of maltose produced in the analytical procedure by a substance containing a given amount of alpha-amylase (and therefore its measured activity in amylase activity units) can vary considerably as a result of slight variations in the test conditions or in the substances with which the alpha-amylase is associated. The activity of a particular sample can be measured consistently and reproducibly, and values such as those for the percentage amylase activity remaining after a storage test are reliable. While the numerical values of amylase activity quoted in this specification indicate the order of magnitude and are self-consistent, they should not be taken to be exact in absolute terms.

Alpha-amylases vary in activity depending upon their purity and pH in solution. Pure alpha-amylase has a specific activity of about 11,500,000 units per gram, while commercially available preparations varying in content of alpha-amylase have specific activities of about 50,000 to about 1,500,000 amylase activity units per gram. The enzyme-containing detergent compositions of the present invention which contain from 0.0005 percent to 3 percent by weight alpha-amylase (calculated on the basis of pure alpha-amylase) generally contain from about 60 to about 400,000 amylase activity units per gram of detergent composition.

Commercial alpha-amylase compositions which can be utilized in this invention include Wallerstein Bacterial alpha-amylase, Wallerstein Company, Staten Island, New York; alpha-amylase, Miles Chemical Company, Elkhart, Indiana; the alpha-amylase which is an integral part of CRD Protease (Monsanto DA 10) derived from *Bacillus subtilus*, Monsanto Company, St. Louis, Missouri, alpha-amylase, Midwest Biochemical Company, Milwaukee, Wisconsin; bacterial alpha-amylase and fungal alpha amylase, Novo Industri A/S Copenhagen, Denmark, MAXAMYL, Koninklijke Nederlandse Gist- en Spiritusfabriek N.V., Delft, The Netherlands; AMYLASE THC-250, Societe Rapidase, Seclin, France. Mixtures of these materials can be employed in the exercise of the present invention. Mixtures of alpha-amylase and certain alkaline proteases in weight ratios of about 30:1 to about 1:1 of proteases to alpha-amylase have particularly superior cleaning and stain removal properties when incorporated into granular detergent compositions. Preferably such proteolytic

enzymes when employed do not contain disulfide links or sulfhydryl groups.

The alpha-amylase weight content of commercial alpha-amylase compositions usually varies from about 0.5 percent to about 15 percent although some purer grade compositions have a higher alpha-amylase content. The amount of alpha-amylase composition which is used depends on its specific activity. More of an alpha-amylase composition containing 0.5 percent alpha-amylase is required in the detergent compositions of this invention than of an alpha-amylase composition having a higher specific activity.

The inert carriers in which alpha-amylase is generally sold include starch, calcium and sodium sulfate, sodium chloride and sodium tripolyphosphate. The glucose polymers are added to the detergent compositions of this invention in addition to any starch which is present in the inert carrier.

The glucose polymers with an alpha-1,4 main linkage are incorporated into the compositions of this invention is such an amount that the weight ratio of said ingredient to pure alpha-amylase is from about 1:1 to about 5,000:1, preferably from about 8:1 to about 500:1. The glucose polymers suitable for use in the compositions of this invention are carbohydrates which yield a large number of mono-saccharide (glucose) molecules on hydrolysis. Well known examples of compounds belong to the general class of glucose polymers with an alpha-1,4 main linkage are starch, dextrin and glycogen. Starch consists of two fractions, one being known as alpha-amylose and the other as beta-amylose or amylopectin; the former constitutes 10 to 20 percent of starch and the latter 90 to 80 percent. Alpha-amylose is water-soluble; it has apparently a straight-chain configuration with approximately 2,000 glucose units in a polymer molecule. Amylopectin has a branched-chain structure and its average molecule contains about 100,000 glucose units in a polymer molecule. Dextrin and glycogen are both branched polymers containing approximately from 20–100, and approximately 100,000 glucose unit respectively in a polymer molecule.

Although the stabilizing effect of the glucose polymers (in combination with the derivatives of monosaccharides) is obtained from all glucose polymers with an alpha-1,4 main linkage, optimum stabilization is attained by the use of those compounds containing a branched-chain molecular structure. The most preferred glucose polymer is dextrin. By way of example, it can be produced from dry roasted starch by various degradation-recombination reactions. Obviously, the properties of the dextrin obtained are more or less different from each other depending on the technique used for preparing the polymer. The species known as white dextrin is prepared by hydrolytic breakdown of starch in the presence of moisture and high acidity at about 150° C. Yellow dextrin is prepared in the same manner from starch at temperatures from 150° to 200° C with moderate acidity and low moisture (as compared to the method for preparing white dextrins). Dextrin species prepared by molecular rearrangement and repolymerization techniques are also well known and suitable for use.

The derivatives of monosaccharides which are used in this invention in conjunction with the glucose polymers have the general formula $R_1 - (CHOH)_n - Y$ wherein Y represents a salt- or an ester-radical derived from a carboxylic radical; wherein n is 3 or 4, and R_1 is CH_2OH or CHO. They are used in a weight ratio of derivatives of monosaccharides to glucose polymers of from 2:1 to 1:100, preferably from 1:1 to 1:10. Specific examples of compounds suitable for use are the alkali metal and alkaline-earth metal salts of gluconic acid and glucuronic acid. The esters obtained from these latter acids with mono- or polyol bearing compounds are also suitable. Preferred for use in the compositions of this invention are the alkaline-earth metal salts of gluconic acid and particularly calcium gluconate.

In addition to the enzymes and the stabilizing mixture, consisting of a glucose polymer and a derivative of monosaccharides, the detergent compositions of this invention can also contain the usual ingredients which are currently incorporated into detergent compositions. Anionic and nonionic organic detergents, organic and inorganic builders, suds depressors, bleaching compounds, antiflocculating agents, brighteners, dyes, perfumes, and so on can be used.

The detergent composition of the present invention contains from about 1 percent to about 50 percent of an organic synthetic detergent, preferably from about 5 percent to about 30 percent. Organic detergents suitable for use in the stable detergent compositions of the present invention include water-soluble anionic soap and non-soap detergents, nonionic synthetic detergents, zwitterionic synthetic detergents and ampholytic synthetic detergents. Mixtures of such detergents are also effective and can be used.

Specific examples of suitable detergent compounds which can be employed in accordance with the present invention are the following :

water-soluble soaps, such as the sodium, potassium, ammonium and alkanol-ammonium salts of higher fatty acids (C_{10}—C_{22}), and, particularly sodium and potassium tallow and coconut soaps.

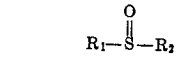
anionic synthetic non-soap detergents, which can be represented by the water-soluble salts of organic sulfuric acid reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical seiected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Examples of these are the sodium or potassium alkyl sulfates, derived from tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, sodium alkyl glyceryl ether sulfonates, sodium coconut oil fatty acid monoglyceride sulfonates and sulfates ; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol and about 1 to 6 moles of ethylene oxide; sodium or potassium alkyl phenol ethylene oxide ether sulfonates, with 1 to 10 units of ethylene oxide per molecule and wherein the alkyl radicals contain from 8 to 12 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide, sodium or potassium salts of fatty acid amide of a methyl tauride; sodium and potassium salts of SO_3— sulfonated C_{10} — C_{24} alpha-olefins;

nonionic synthetic detergents made by the condensation of alkylene oxide groups with an organic hydrophobic compound. Typical hydrophobic groups include condensation products of propylene oxide with propylene glycol, alkyl phenols, condensation product of propylene oxide and ethylene diamine,

aliphatic alcohols having 8 to 22 carbon atoms and amides of fatty acids.

Also nonionic detergents such as amine oxides, phosphine oxides and sulfoxides having semipolar characteristics can be used. Specific examples of long chain tertiary amine oxides include dimethyldodecylamine oxide and bis-(2-hydroxyethyl) dodecylamine. Specific examples of suitable phosphine oxides are found in U.S. Pat. No. 3,304,263 which issued February 14, 1967, and include : dimethyldodecylphosphine oxide and dimethyl-(2-hydroxydodecyl) phosphine oxide.

The suitable long chain sulfoxides correspond to the formula



wherein R_1 and R_2 are substituted or unsubstituted alkyl radicals, the former containing from about 10 to about 28 carbon atoms, whereas R_2 contains from 1 to 3 carbon atoms. Specific examples of these sulfoxides are : dodecyl methyl sulfoxide and 3-hydroxy tridecyl methyl sulfoxide.

examples of *ampholytic synthetic detergents* are sodium 3-dodecylaminopropionate and sodium 3-dodecylaminopropane sulfonate.

useful *zwitterionic synthetic detergents* are 3-(N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy propane-1-sulfonate.

Preferred organic detergents include sodium alkyl benzene sulfonate, sodium alkyl sulfate, and mixtures thereof wherein the alkyl group is of branched or straight chain configuration and contains about 10 to about 18 carbon atoms.

The alkaline detergency builders can be employed in a detergent composition of the present invention in a weight ratio or organic detergent to alkaline builder of about 10:1 to about 1:30, preferably 5:1 to 1:20.

The builders can be inorganic or organic in nature and can be selected from a wide variety of known builder materials. Useful alkaline inorganic builders are alkali metal carbonates, phosphates, polyphosphates, and silicates. Specific examples of such salts are sodium and potassium tripolyphosphates, carbonates, phosphates and hexametaphosphates. Useful alkaline organic builders are alkali metal, ammonium and substituted ammonium polyphosphonates, polyacetates and polycarboxylates. The polyphosphonates specifically include the sodium and potassium salts of ethylene diphosphonic acid, sodium and potassium salts or ethane-1-hydroxy-1,1-diphosphonic acid and sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Other examples include the water-soluble salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxymethonediphosphonic 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.

Polyacetate builder salts useful herein include the sodium, potassium, lithium, ammonium, and substituted ammonium salts of the following acids : ethylenediaminetriacetic acid, N-(2-hydroxyethyl)-nitrilodiacetic acid, diethylenetriamine-pentaacetic acid, 1,2-diaminocyclo-hexanetetraacetic acid and nitrilotriacetic acid. The trisodium salt of the last acid is generally and preferably utilized herein.

The polycarboxylate builder salts useful herein consist of water-soluble salts of polymeric aliphatic polycarboxylic acids of the type described in U.S. Pat. No. 3,308,067. Examples include sodium polyitaconate and sodium polymaleate.

The oxidizing bleach embodiments of the present invention are so-called "peroxygen" bleaching agents, of which sodium and potassium perborate are the best known. Other peroxygen compounds having bleaching power, however, can also be used. For example, customary inorganic peroxy compounds such as other alkali metal perborates, percarbonates, and monopersulfates are useful. In addition, other examples are hydrogen peroxide and alkali metal peroxides such as sodium, potassium and lithium peroxide.

The bleaching effectiveness of peroxygen bleaches can be improved, particularly at lower washing temperatures by the addition of activators. Examples of especially effective bleach activators are triacetyl cyanurate, tetraacetyl methylene diamine, sodium and potassium acetoxy benzene sulfonate, phthalic anhydride, and benzoyl imidazole.

The retention of the amylolytic activity during storage in granular detergent compositions containing a mixture of glucose polymers and derivatives of monosaccharides is illustrated by the following series of examples. In all examples, the detergent compositions are packed in the usual cardboard cartons and submitted to a storage test as described in the individual examples.

EXAMPLE I

A granular detergent composition having the following formula is prepared by a conventional spray-drying technique:

Ingredients	Composition in parts by weight
Sodium salt of linear dodecylbenzenesulfonate	9
Condensate of tallow alcohol with 11 moles of ethylene oxide	2
Fatty acid derived from C_{14-28} hydrogenated fish oil	3
Anhydrous sodium tripolyphosphate	31
Alkaline silicate solution; ratio $Na_2O:SiO_2$ = 2.2:1	9
Sodiusm sulfate	6
Minor ingredients and moisture	5

65 parts of these detergent base granules are dry-mixed with 32 parts commercial grade sodium perborate and with 3 parts of agglomerates A or B or C.

These agglomerates are prepared in dry-mixing the amounts of anhydrous sodium tripolyphosphate and proteolytic enzyme preparation (ALCALASE) given in the table below. A slurry containing the respective amounts of partially hydrolyzed collagen, amylolytic enzyme preparation (AMYLASE-THC-250), water and, if any, dextrin and calcium gluconate is sprayed onto the (dry) mixture of anhydrous sodium tripolyphosphate and proteolytic enzyme preparation thereby using the technique disclosed in U.S. Pat. No. 3,451,935.

Compositions of agglomerates A, B and C are as follows (expressed in % by weight of total agglomerate).

	A	B	C
Anhydrous sodium tripolyphosphate	76.5	79	77
Proteolytic enzyme preparation ALCALASE containing 4.0 AU/g*	7.5	7.5	7.5

partially hydrolyzed collagen COLLOID 1-V-Technical Protein Colloid supplied by Swift & Company Chicago, USA	2.5	2.5	2.5
Amylolytic enzyme preparation AMYLASE-THC-250 containing 4.3 × 105 MU/g	1	1	1
MW 2280 commercial dextrin, manufactured by Scholten's Fabrieken — The Netherlands	2		2
Ca-gluconate	0.5		
water	10	10	10

* ANSON, Journ. Gen. Physiol. 22, 79 (1939)

Samples having the composition described herebefore are storage tested at 35° C and 80 percent relative humidity. The percent of remaining amylolytic activity is determined by analytical assays.

Storage time in weeks	% Remaining amylolytic activity in detergent sample containing agglomerate	
	A	B
1	77	38
2	60	17
3	50	1

The retention of the amylolytic activity is clearly illustrated in the preceding table. It is noteworthy seeing how the rate of deactivation in the inventive compositions tends to level whereas identical compositions which do not contain the mixture of dextrin and calcium-gluconate tend to completely loose their initial activity.

EXAMPLE II

A. Detergent samples having the composition of example I are submitted to storage tests with different sets of parameters as indicated below. The retention of the amylolytic activity is determined by analytical assays.

Storage conditions			Percent remaining amylolytic activity after—							
			Weeks			Months				
Temp., ° C.	Relative humidity, percent	Agglomerate	1	2	3	1	2	3	4	5
35	80	A	80	63	51					
35	80	C	57	39	33					
35	80	B	38	16	2					
20	80	A				87	79	73	68	64
20	80	C				75	62	52	43	36
20	80	B				72	54	40	28	17
25	35	A				89	79	69	60	
25	35	C				73	60	50	42	
25	35	B				63	45	33	23	

B. The same detergent compositions as described under A. of this example are storage tested at 20° C and 80 percent relative humidity. The remaining amylolytic activity is determined by stain removal testing. To this effect, cotton swatches are impregnated with a solution or slurry of gelatinized starch and black ink. These impregnated swatches are then heated to 100° C. This heat treatment serves to make the swatches better suitable for the quantitative amylase evaluation.

The stain removal tests are made in a launderometer (Atlas LHDEF, manufactured by Atlas Electric Devices Co., Chicago, Illinois). The testing conditions are:

pH of laundry solution : 9.0

two swatches (4 × 4 cm) per 500 ml jar,

detergent usage concentration : 0.6 gram per liter, heat-up cycle (20° to 100° C).

A calibration curve is prepared using freshly prepared detergent compositions as described in example I with varying levels of alpha-amylase. The performance of test samples after storage is plotted on the calibration curve to determine the remaining alpha-amylase activity.

The reflectance of the starch-ink cotton swatches is measured, after launderometer treatment, with an EEL spectro-photometer (Evan's Electroselenium Ltd.); filter No. 603 is used. The reflectance measurements are converted into alpha-amylase concentrations by comparison with the calibration curve prepared as described herebefore.

Storage time (in months)	% Remaining amylolytic activity in detergent sample containing agglomerate		
	A	B	C
1	91	70	76
2	82	53	62
3	72	38	52
4	63	26	42
5	54	17	35

These test results are in agreement with the experimental data given in part A. of this example, i.e., the retention of the amylolytic activity of detergent compositions containing a mixture of glucose polymer and and calcium gluconate is superior to what can be obtained from the addition of dextrin only.

EXAMPLE III

Detergent composition samples as described in example I are storage tested to determine the influence of calcium gluconate on the retention of amylolytic activity. The evolution in amylolytic activity is determined by analytical assays.

Storage conditions				Percent remaining amylolytic activity after—						
				Weeks				Months		
Temp., ° C.	Relative humidity, percent	Agglomerate	Gluconate, percent by wt.	1	2	3	4	1	2	3
20	80	A	0.5					87	83	79
20	80	A	1.0					92	85	78
20	80	B	1.0					54	32	20
20	80	B						54	33	21
35	80	A	0.5	65	53	47	43			
35	80	A	1.0	67	54	44	39			
35	80	B	1.0	11	0					
35	80	B		11	0					

These test results reveal that the attainment of optimum results depends on the relative quantity of the gluconate and the dextrin. It appears, that, in this example, the use of 1 percent instead of 0.5 percent of gluconate does not substantially improve the performance of these compositions.

EXAMPLE IV

Detergent samples having the composition of example I and containing in addition 0.5 percent of sodium thiosulfate are storage tested. The residual amylolytic activity rexpressed in percent is determined by analytical assays.

Storage conditions		Agglomerate	% Remaining amylolytic activity after months				
temp. °C	relative humidity %		1	2	3	4	5
20	80	B	65	36	21	10	3
20	80	A	74	51	35	24	15
25	35	B	64	47	33		
25	35	A	74	58	46		

Storage conditions		Agglomerate	% Remaining amylolytic activity after weeks		
temp. °C	relative humidity %		1	2	3
35	80	B	57	27	3
35	80	A	79	57	46

Substantially similar levels of residual amylolytic activity are found in substituting the dextrin in agglomerate A by the same quantity of amylopectin or by a mixture of amylopectin and wheat flour in a weight ratio of 1:1.

What is claimed is:

1. A granular detergent composition consisting essentially of:

a. an organic synthetic detergent selected from the group consisting of water-soluble soaps, anionic synthetic non-soap detergents, nonionic synthetic detergents, ampholytic synthetic detergents, zwitterionic synthetic detergents, and mixtures thereof;

b. an alkaline builder selected from the group consisting of an organic sequestering builder, an inorganic alkaline builder and mixtures thereof, the proportion of said detergent to said builders being in the range of from about 10:1 to 1:30;

c. glucose polymers with an α-1,4 main linkage selected from the group consisting of starch, dextrin and glycogen in a weight ratio of said ingredient to pure α-amylase of 1:1 to 5000:1;

d. a monosaccharide derivative compound; selected from the group consisting of the alkali metal and alkaline earth metal salts of gluconic acid and glucuronic acid; whereby the weight ratio of this compound to said glucose polymers is from 2:1 to 1:100; and

e. from 0.0005 percent to about 3 percent of α-amylase calculated on the basis of pure α-amylase.

2. The granular detergent composition of claim **1** wherein the proportion of said detergent to said builder is in the range of from about 5:1 to about 1:20.

3. The granular detergent composition of claim **1** wherein dextrin is used as the glucose polymer and whereby the weight ratio of dextrin to pure α-amylase is from 8:1 to 500:1.

4. The granular detergent composition of claim **1** wherein the monosaccharide derivative compound is an alkali metal or alkaline earth metal salt of gluconic acid.

5. The granular detergent composition of claim **4** wherein the salt of gluconic acid is a divalent salt and whereby the weight ratio of salt to glucose polymer is from about 1:1 to 1:10.

6. The granular detergent composition of claim **5** wherein the divalent salt of gluconic acid is calcium gluconate.

7. The granular detergent composition of claim **1** wherein from 0.001 percent to 0.010 percent by weight of pure α-amylases are used.

8. The granular detergent composition of claim **14** wherein from 0 percent to about 5 percent by weight of partially hydrolyzed collagen is used.

9. The granular detergent composition of claim **1** wherein sodium tripolyphosphate is used as the alkaline builder material.

10. The granular detergent composition of claim **1** further comprising from 0 percent to about 50 percent of a peroxy-bleach compound selected from the group consisting of alkali metal perborates, percarbonates and monopersulfates, hydrogen peroxide and alkali metal peroxides.

11. The granular detergent composition of claim **10** wherein the peroxybleach compound is a perborate.

12. The granular detergent composition of claim **1** further comprising from 0 to 5 percent of proteolytic enzymes.

13. The granular detergent composition of claim **12** wherein up to 2 percent of a proteolytic enzyme is used.

14. The granular detergent composition of claim **12** wherein the proteolytic enzymes used do not contain disulfide links or sulfhydryl groups.

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