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3,803,285

EXTRUSION OF DETERGENT COMPOSITIONS

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No Drawing. Filed Jan. 20, 1971, Ser. No. 108,178

Int. Cl. C11d 3/22, 11/00

U.S. Cl. 264-143

1 Claim

ABSTRACT OF THE DISCLOSURE

Novel detergent compositions comprising from about 10% to about 90% detergent surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic detergent surfactant and mixtures thereof, and from about 10% to about 90% modified carbohydrate.

BACKGROUND OF THE INVENTION

From time to time compositions have been disclosed which comprise detergent and starch. For example, U.S. Pat. 3,210,287 discloses a liquid detergent composition comprising a nonionic detergent and starch and U.S. Pat. 2,195,512 discloses compositions comprising anionic detergent and starch. In the art, the unqualified term starch refers to naturally occurring starch granules isolated from vegetable raw materials. While such starches can be useful in some detergent compositions, for example detergent bars, they are not water soluble and are not generally suitable for use in granular detergent compositions formulated especially for laundry use.

In addition certain modified water soluble starches have been suggested for use in detergent compositions. For example, British Pat. 971,659 discloses that water soluble, low viscosity starch phosphates are useful detergent builders and antiredeposition agents and can be incorporated into detergent compositions.

The use of phosphate compounds in detergent composition, however, can be undesirable because in some areas the spent detergent is discharged into lakes and phosphates can contribute to eutrophication of lakes. In addition starch phosphates can form undesirable precipitates with the hardness ingredients in water, which can adversely affect fabrics being laundered.

Granular detergent compositions generally comprise in addition to detergent large amounts of inorganic alkali metal salts, as for example, sodium tripolyphosphate, sodium carbonate and sodium sulfate. Such salts can be useful adjuvants in detergent compositions in that the salts can function as builders to increase the detergency of the composition. In addition, inorganic salts, especially hydratable inorganic salts, can significantly aid the formation of dry, free-flowing granular detergent compositions.

While the use of alkali metal inorganic salts in detergent compositions can present the advantages noted above, the use of these salts can also present certain disadvantages. For example, such salts can form undesirable precipitates with the constituents of hard water. These precipitates can deposit on a fabric being laundered and can cause the fabric to exhibit a dull appearance. In addition, the inorganic phosphate salts can be undesirable because of eutrophication problems.

An especially desirable detergent composition is a detergent composition which can be formulated into suitable detergent granules without the inclusion of inorganic salts.

SUMMARY OF THE INVENTION

This invention presents detergent compositions comprising from about 10% to 90% detergent surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic detergent surfactants and mix-

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tures thereof, and from about 10% to 90% of modified carbohydrate selected from the group consisting of

(I) pregelatinized starch derivatives having a minimum Scott viscosity of about 60 g. to about 100 g. or greater at flow rates of from about 40 to about 80 seconds, said starch derivatives being selected from the group consisting of

(a) hydroxyalkyl starch ethers having a D.S. of from about 0.01 to about 0.5 wherein the alkyl group is selected from the group consisting of ethyl, propyl, butyl and di-hydroxypropyl;

(b) starch esters having a D.S. of from about 0.01 to about 0.5, said starch esters being selected from the group consisting of starch acetate, starch propionate, starch butyrate, starch succinate and starch maleate;

(c) oxidized starch;

(II) dextrans; and

(III) starch hydrolysates having a D.E. of from about 2 to about 35.

These compositions exhibit good detergent properties, and can be formulated into particularly desirable detergent granules.

DESCRIPTION OF THE INVENTION AND ITS PREFERRED EMBODIMENTS

This invention presents novel detergent compositions which are especially useful in laundering fabrics. The novel detergent compositions of this invention comprise from about 10% to 90% detergent surfactant and from about 10% to about 90% the modified carbohydrate as herein defined. Preferably the detergent compositions of this invention comprise from about 10% to 70% detergent surfactants and from about 30% to about 90% modified carbohydrate.

The detergent surfactants useful in this invention consist of anionic, nonionic, zwitterionic, ampholytic detergent surfactants and mixtures thereof.

Examples of suitable detergent surfactants include the following:

(a) Anionic detergent surfactants such as soap wherein the fatty acids contain from about 8 to about 22 carbon atoms and wherein the cation is selected from the group consisting of sodium, potassium, ammonium and substituted ammonium cations. Specific examples are the ordinary alkali metal soaps such as the sodium and potassium salts of the higher fatty acids of naturally occurring plant or animal esters (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease and lard, and mixtures thereof) or of synthetically produced fatty acids (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process), of resin acid (e.g., rosin and those rosin acids in tall oil) and/or of naphthenic acids. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process.

Especially suitable anionic detergent surfactants include synthetic anionic detergents characterized by their high solubility in water, their resistance to precipitation by the constituents of hard water and their surface active and effective detergent properties.

These anionic synthetic detergents include the water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in the 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 syn-

thetic detergents which form a part of the preferred compositions of the present invention are the sodium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkylbenzenesulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, for example those of the types described in United States Letters Patent Nos. 2,220,099, and 2,477,383; sodium alkylglycerylethersulfonates, 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 salt of alkylphenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 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 methyltauride in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specially set forth in United States Letters Patent Nos. 2,486,921, 2,486,922 and 2,396,278.

(b) Nonionic synthetic detergents: This class of synthetic detergents may be broadly defined as compounds aliphatic or alkyl aromatic in nature which do not ionize in water solution.

For example, a well known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with an 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 1200 to 2500. 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 polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergent include:

(1) The polyethylene oxide condensates of alkylphenols, e.g., the condensation products of alkylphenols or dialkylphenols wherein the alkyl group contains from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide is being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkylphenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, n-octene, or n-nonene, for example.

(2) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. 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 ethylenediamine and excess propylene oxide; bases having a molecular weight of the order of 2500 to 3000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(4) Long chain tertiary amine oxides corresponding to the following general formula, $R_1R_2R_3N \rightarrow O$, wherein

R_1 is an alkyl radical of from about 8 to 18 carbon atoms, and R_2 and R_3 are each methyl or ethyl radicals. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethyldecylamine oxide, dimethyltetradecylamine oxide, dimethylhexadecylamine oxide.

(5) 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 18 carbon atoms in chain length and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphine oxides are:

Dimethyldodecylphosphine oxide,
Dimethyltetradecylphosphine oxide,
Ethylmethyltetradecylphosphine oxide,
Cetyldimethylphosphine oxide.

(c) Ampholytic synthetic detergents: This class of synthetic detergents can be broadly described as derivatives of aliphatic amines which contain a long chain of about 8 to 18 carbon atoms, and an anionic water solubilizing group, e.g., carboxy, sulfo, or sulfato. Examples of compounds falling within this definition are sodium-3-dodecylaminopropionate and sodium-3-dodecylaminopropane-sulfonate.

(d) Zwitterionic synthetic detergents: This class of synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium compounds, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo or sulfato. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio)-propane and 3-(N,N-dimethyl-N-hexadecylammonio) 2-hydroxypropane-1-sulfonate.

The anionic, nonionic, ampholytic and zwitterionic detergent surfactants mentioned above can be used singly or in combination in the practice of the present invention. The above examples are merely specific illustrations of the numerous detergents which can find application within the scope of this invention.

It has been found that certain particular modified carbohydrates are suitable for use in the detergent compositions of this invention. Among the suitable modified carbohydrates are:

(I) pregelatinized starch derivatives having a minimum Scott viscosity of greater than about 60 g. to about 100 g. or greater at flow rates of from about 40 to about 80 seconds, said starch derivatives being selected from the group consisting of

(a) hydroxyalkyl starch ethers having a D.S. of from about 0.01 to about 0.5 wherein the alkyl group is selected from the group consisting of ethyl, propyl, butyl and dihydroxypropyl;

(b) starch esters having a D.S. of from about 0.01 to about 0.5, said starch esters being selected from the group consisting of starch acetate, starch propionate, starch butyrate, starch succinate and starch maleate;

(c) oxidized starch;

(II) dextrans; and

(III) starch hydrolysates having a D.E. of from about 2 to about 35.

The modified carbohydrates useful herein can be derived from parent starches having root and cereal origin. Preferred parent starches are those derived from corn, wheat, milo and potato. Especially preferred parent starches are the waxy starches, as for example those derived from waxy milo and waxy corn.

The pregelatinized starch derivatives useful herein are well known. The pregelatinized starch derivatives are obtained by cooking the starch derivative, as for example at temperatures of about 170° F. to 300° F., according to known processes to obtain starch derivatives having the Scott viscosities required herein. (Processes for pregelatinizing starch derivatives are disclosed in *Starch: Chemistry and Technology*, vol. II, edited by Whistler and Paschall, copyright 1967 by Academic Press at pp. 178-9 and 523-8; the method for determining Scott viscosity is described in *Chemistry and Industry of Starch*, by Kerr, 2nd ed., copyright 1950 by Academic Press.)

The starch derivatives useful herein are well known. The hydroxyalkyl starch ethers and starch esters can be obtained by known etherification and esterification processes. These starch ethers and esters should have a D.S. of about 0.01 to about 0.5, and preferably about 0.1 to about 0.5. As used herein D.S. means the average degree of substitution of starch hydroxyl groups per anhydroglucose unit of the chemical modifying substituent, as for example a hydroxyalkyl or carbonyl group. Oxidized starch can be obtained by known processes involving oxidation of starch with a suitable oxidizing agent, as for example sodium hypochlorite, potassium dichromate and sodium permanganate. The starch can be oxidized under acid, alkaline or neutral conditions, and the resulting product can contain carboxyl and carbonyl groups. Preferably the oxidized starch has a D.O. of 0.01 to 1.0, where D.O. refers to the number of carboxyl groups introduced per anhydroglucose unit. (These starch derivatives and methods for obtaining them are discussed in *Starch: Chemistry and Technology*, vol. I, edited by Whistler and Paschall, copyright 1965 by Academic Press at pp. 458-78.)

Dextrins are polysaccharide products of a complex nature resulting from the partial degradation of starch, such as corn starch, potato starch, wheat starch, etc., with heat, as for example, by roasting with acid or alkaline catalysts. Linear and branched dextrins are classified in three types. The particular type obtained depends on the heating time, temperature, and catalyst employed in the treatment of the starch. These types are classified as white dextrins, yellow or canary dextrins, and British gums, and all such dextrins are suitable herein. White and canary dextrins are preferred in that British gums are brown in color. White dextrins are preferably pregelatinized (made water soluble during manufacture), if necessary, to render them more compatible with detergent components. Dextrins and methods for obtaining them are well known. See, for example *Starch: Chemistry and Technology*, vol. I, op. cit., p. 421 ff, and vol. II, op. cit., p. 253 ff.

The starch hydrolysates useful in the compositions of this invention are a relatively new class of starch materials. These starch hydrolysates are made by subjecting a source of starch, such as hereinbefore mentioned, to enzyme or acid treatment or a combination of both. It is important that the starch hydrolysate have a relatively low D.E. (Dextrose equivalent). The starch hydrolysate should have a D.E. of from about 2 to about 35, and preferably have a D.E. of from about 5 to about 25. The most preferred materials have a D.E. within the range of 5 to 15. Starch hydrolysates of this type have been found to be excellent agents for forming the detergent compositions of this invention. In particular, these starch hydrolysates are surprisingly useful in reducing moisture pick-up of normally hygroscopic detergent surfactants and builders, and are surprisingly detergent compatible.

The term D.E. is used herein to refer to the reducing sugars content of the dissolved solids in a starch hydrolysate expressed as percent dextrose as measured by the Luff-Schoorl method (NBS Circular C-40, p. 195 as appearing in *Polarimetry, Saccharimetry, and the Sugars*; authors Frederick J. Bates and Associates).

The starch hydrolysates for use in the present invention can be made by several methods.

One method involves a one step enzyme technique wherein a starch such as a waxy starch is treated with a single enzyme application of bacterial alpha amylase. More specifically, an aqueous slurry of a waxy starch, having a solids content less than 50%, is subjected to the hydrolytic action of bacterial alpha amylase under suitable conditions of fermentation to produce a starch hydrolysate. This method is specifically illustrated hereinafter in the description designated as Method A.

The same product as described above, may also be made via a number of other routes, as for example in a process involving a two step enzyme technique. For example, a mixture of starch and water having a solids content less than 50% may be first subjected to the hydrolytic action of a bacterial alpha amylase followed by a high temperature heating step to solubilize any unsolubilized starch. Since this temperature tends to inactivate the enzyme it is then necessary to cool the solubilized partial hydrolysate and subject it to a second hydrolysis by treatment with additional bacterial alpha amylase to obtain the final starch hydrolysate. This technique is specifically illustrated hereinafter in the description designated as Method B.

A third method for obtaining low D.E. starch hydrolysates involves a two step acid enzyme technique. This process comprises hydrolyzing a mixture of starch and water by the action of acid to reach a D.E. between about 5 and about 15. The partial hydrolysate is subsequently subjected to the action of bacterial alpha amylase to obtain a starch hydrolysate having a D.E. of from about 10 to about 25.

It has been surprisingly found that the detergent compositions of this invention are especially suitable for preparing highly desirable detergent granules. These highly desirable detergent granules exhibit unexpectedly high bulk densities, and are surprisingly free-flowing and resistant to caking. In addition, detergent granules employing the compositions of this invention can be prepared which are unexpectedly strong in that they exhibit a low degree of friability. These detergent granules can be especially desirable since they dissolve in water rapidly. This surprising characteristic of the novel detergent granules is especially advantageous in home laundry situations.

The modified carbohydrates useful in this invention are remarkably detergent compatible in that they do not adversely affect the detergency of the detergent surfactants useful in this invention. Generally these modified carbohydrates contribute to the detergency of the detergent surfactant, and inhibit redeposition.

The detergent compositions of this invention are especially amenable to the inclusion of detergent adjuvants. For example, novel detergent formulations employing the novel detergent compositions of this invention can contain from 0% to about 80% detergent adjuvants, by weight of the novel detergent formulation. Especially suitable detergent adjuvants include builders, alkaline material, anti-redeposition agents, optical brighteners, bleaching agents, perfumes, dyes and anti-corrosion compounds.

Suitable builders can include inorganic and organic builders. Examples of suitable inorganic builders are alkali metal, carbonates, phosphates, polyphosphates and silicates. Specific examples of such builders are sodium and potassium tripolyphosphates, carbonates, pyrophosphates, phosphates and hexametaphosphates.

Examples of suitable organic builder ingredients are (1) alkali metal amino polycarboxylates (e.g., sodium and potassium ethylene diaminetetraacetates, N-(2-hydroxyethyl)-ethylene diaminetriacetates, nitrilotriacetates, and N-(2-hydroxyethyl)-nitrilo diacetates); (2) alkali metal salts of phytic acid (e.g., sodium and potassium phytates—see U.S. Pat. 2,739,943); (3) water-soluble ethane-1-hydroxy-1,1-diphosphonates (e.g., preferably the trisodium and tripotassium salts—see U.S. Pat. 3,159,581); (4) water-soluble salts of methylene diphosphonic acid (e.g., trisodium and tripotassium methylene diphos-

phonate and other salts described in U.S. Pat. 3,213,030); (5) water-soluble salts of substituted methylene diphosphonic acids (e.g., trisodium and tripotassium ethylidene, isopropylidene, benzylmethylidene and halomethylidene diphosphonates and the other substituted methylene diphosphonates disclosed in U.S. Pat. 3,422,021); (6) water-soluble salts of polycarboxylic acid polymers and copolymers as described in U.S. Pat. 3,308,067 (e.g., 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 (7) cycloalkane polycarboxylic acids (e.g., cyclopropane-1,1,2-tricarboxylic acid) such as disclosed in U.S. Pat. 3,459,670.

Mixtures of any and all of the organic and/or inorganic builders can be used and can be desirable. Suitable mixtures include tertiary mixtures of sodium tripolyphosphate, sodium nitrilotriacetate and sodium ethane-1-hydroxy-1,1-diphosphonate as disclosed in U.S. Pat. 3,392,121. An especially suitable builder is a binary mixture containing sodium nitrilotriacetate and sodium ethane-1-hydroxy-1,1-diphosphonate.

Excellent built granular detergent products comprise from about 10% to about 85% detergent surfactant useful herein, from about 10% to about 85% modified carbohydrate useful herein, and from about 5% to about 80% builder. Preferably these novel built granular detergent products contain about 15% to about 30% builder, and about 20% to about 40% modified carbohydrate.

While inorganic builders can be included in the compositions of this invention, the preferred builders are the organic builders, especially the organic builders which are sequesterants, as for example, the organic builders hereinbefore mentioned. The usual adjuvants can be employed with the built detergent product.

It has been surprisingly found that excellent built granular detergent products can be formed wherein the builder is an organic sequesterant builder. Such products can be especially desirable laundry compounds since neither the builder nor the starch components are insolubilized by the hardness ingredients in water, as for example calcium ions.

The phosphate builders are not preferred for the reasons hereinbefore mentioned and can be avoided or employed sparingly. The detergent compounds of this invention are especially desirable in that excellent granular detergent products can be formed containing no inorganic salts, as for example inorganic builders such as inorganic phosphate salts.

It should be recognized, however, that it is often expedient to incorporate inorganic salts in detergent compositions. For example, inorganic salts can be excellent inexpensive builders. In addition, inorganic salts are often formed in processes for forming the detergent surfactant, and processes for separating the detergent surfactant and inorganic salt can be difficult. While the compositions of this invention admit the inclusion of inorganic salts, they permit the inclusion of such salts at low levels.

Specific examples of other especially desirable adjuvants include alkaline material, such as sodium hydroxide or potassium hydroxide, as supplementary pH adjusters, and corrosion inhibitors such as water soluble sodium and potassium silicates. Desirably the detergent composition presents a pH of from about 9 to 11 in water containing a suitable dosage for cleaning and laundering. Sodium sulfate, sodium carbonate and moisture can be included in the compositions of this invention.

Detergent granules comprised of the detergent compositions of this invention can be formed by several different methods. For example, the detergent composition can be mixed with an amount of water to form a slurry, and the slurry can be spray dried according to known techniques. Preferably the pregelatinized starches used herein are formed by adding the starch derivatives to the

slurry, and heating the slurry for a suitable time to gelatinize the starch derivative in situ.

Spray drying the detergent composition generally involves forming a slurry with at least a sufficient amount of water such that the resulting slurry can be sprayed from atomizing nozzles. The detergent compositions of this invention, however, can be formed into pumpable plastic compositions by the addition of a very small amount of water, heated in a cooking extruder to a temperature of from about 240° F. to about 300° F., or higher, as for example 400° F., and extruded as a thin ribbon. Since the temperatures of the cooking extruder are sufficient to gelatinize the starch derivatives, preferably the starch derivatives are not pregelatinized prior to the formation of the extruded product. On exposure to the atmosphere, the water in the extruded material vaporizes forming a puffed detergent material which can be broken or cut into suitably sized granules by a breaking or cutting means, as for example by a rotating blade. The granular product can be sized by screening prior to packaging. This novel process can be advantageous since less heat is consumed in vaporizing the water. (Cooking extrusion is well known in the food arts. See, for example, "Continuous Cooking Extrusion: What Is It?" Cereal Science Today, June, 1969.)

The following examples are presented to specifically illustrate the invention disclosed herein.

Examples 1-10

Suitable detergent compositions of this invention employing pregelatinized starch derivatives are provided in the following ten examples.

Example	Percent by weight									
	1	2	3	4	5	6	7	8	9	10
Composition:										
Hydroxyethyl starch, ¹ D.S. 0.07, Scott viscosity 100 g. at 45 seconds	10			40				30		
Starch acetate, ¹ D.S. 0.2, Scott viscosity 20 g. at 60 seconds		80			10				70	
Oxidized starch, ¹ Scott viscosity 60 g. at 37 seconds			40							50
Oxidized starch, ¹ Scott viscosity 100 g. at 45 seconds							30			50
Sodium linear alkylbenzene sulfonate		90	20	60						50
Nonionic ²				60	90	70				
Zwitterionic ³							70	30	50	

¹ Pregelatinized.

² Nonylphenol condensed with about 10 moles of ethylene oxide.

³ 3-(N,N-dimethyl-N-hexadecylammonio)-propane.

Each of the above compositions exhibits excellent detergency.

EXAMPLE 11

Two parts of each of the compositions obtained in Examples 1-10 are mixed with one part water and spray dried. Each of the resulting products obtained is a dry free-flowing granular detergent.

EXAMPLE 12

When in Example 3, canary dextrin is used in place of the oxidized starch, substantially the same results are obtained in that a detergent composition exhibiting excellent detergency is formed.

EXAMPLE 13

When two parts of the detergent composition of Example 12 is mixed with one part water and spray dried, a dry free-flowing granular detergent is obtained.

EXAMPLES 14-19

Part one.—The following specific procedures illustrate three basic methods of making low D.E. starch hydrolysates used in this invention.

Method A—One step enzyme technique

An aqueous starch slurry was prepared containing 30% solids by weight of waxy milo starch. The temperature of the slurry was raised and held between 85° C. and 92° C. A bacterial alpha amylase preparation was added in an amount just above 0.025% by weight of the starch over a period of slightly more than 30 minutes. The mixture was then held at the same temperature for an additional period of 30 minutes. The temperature was then reduced to below 80° C. and the conversion was allowed to continue until the desired D.E. was reached. The temperature of the mixture was then suddenly raised to about 120° C. in order to inactivate the enzyme and terminate the conversion.

Table 1 below sets forth typical saccharide analyses of low D.E. hydrolysates obtained in accordance with the above procedure. DP designates the range of polymerization. DP₁ represents the total quantity expressed in percent by weight dry basis of monosaccharides present in the hydrolysate. DP₂ represents the total quantity of disaccharides present in the hydrolysate and so forth.

TABLE 1.—TYPICAL SACCHARIDE ANALYSES

Hydrolysate composition	D.E.				
	5	10	15	20	25
DP ₁	0.1	0.3	0.7	1.4	2.4
DP ₂	1.3	3.4	5.3	7.6	9.7
DP ₃	1.8	4.3	6.9	9.4	12.0
DP ₄	1.8	3.5	5.2	6.9	8.6
DP ₅	1.8	3.6	5.5	7.4	9.3
DP ₆	3.3	7.0	10.6	14.3	18.0
DP ₇ and higher.....	89.9	77.9	65.6	53.0	40.0

For use in the examples here the product having a D.E. of 5 is employed.

Method B—Two step enzyme-enzyme technique

Unmodified corn starch was slurried in water to provide an aqueous suspension containing 28–32% by weight of the unmodified corn starch. The pH was at 7.5–8.0. To this mixture was added HT-1000 bacterial alpha amylase (manufactured and sold by Miles Chemical Laboratories) in an amount of 0.05% based on starch solids. This starch suspension was added over a 30 minute period to an agitated tank maintained at a temperature of 90–92° C. After completion of starch addition, liquefaction was continued for 60 minutes at which time the hydrolysate was within the D.E. range of 2 to 5. The liquefied starch was then heated to 150° C. and held at this temperature for 8 minutes. The heat treatment destroyed residual enzyme activity and resulted in improved filtration rates and in decreased yield losses upon filtration.

Further saccharification to the final D.E. was accomplished by the addition of more HT-1000 bacterial alpha amylase after cooling the liquefied starch hydrolysate to a suitable temperature for conversion. The liquefied starch was cooled to 80–85° C. and HT-1000 added in an amount of 0.02% by weight starch solids. After 14 to 20 hours of conversion the desired terminal D.E. of 20 was obtained.

The final starch hydrolysate product was analyzed and the following analytical values were obtained.

TABLE 2

D.E.	20.7
DP ₁	2.4
DP ₂	7.5
DP ₃	10.8
DP ₄	8.0
DP ₅	6.8
DP ₆	15.1
DP ₇₊	49.4

Part two.—Suitable detergent compositions of this invention employing the starch hydrolysates of part one are provided in the following six examples. These compositions are formed by mixing together detergent surfactant and starch hydrolysate. Each of the compositions exhibits

good detergency and can be formulated into detergent granules.

Example.....	Percent by weight				
	14	15	16	17	18
Composition:					
Starch hydrolysates A ¹	10				90
Starch hydrolysates B ¹		80		40	
Do. ¹			60		90
Sodium linear alkylbenzene sulfonate.....	90	20			
Nonionic ²			40		10
Zwitterionic ³				60	10

¹ The starch hydrolysate product of the similarly designated method of Part One.

² Nonylphenol condensed with about 10 moles of ethylene oxide.

³ 3-(N,N-dimethyl-N-hexadecylammonio)-propane.

EXAMPLE 20

Two parts of each of the compositions of Examples 13–19 are mixed with 1 part water and spray dried. Each of the resulting products obtained is a dry free-flowing granular detergent.

EXAMPLES 21–28

The following compositions are examples of built detergent compositions:

Example.....	Percent by weight					
	22	23	24	25	26	27
Composition:						
Oxidized starch, ¹ Scott viscosity 100 g. at 45 sec.....						80
Starch hydrolysates A ²		35		40		40
Starch hydrolysates B ²			45			30
Hydroxyethyl starch, ¹ D.S. 0.07, Scott viscosity 100 g. at 45 sec.....				45		
Sodium linear alkylbenzene sulfonate.....		20	20		20	20
Nonionic ³		20				10
Zwitterionic ⁴					10	
Sodium silicate.....	15			15		20
Sodium sulfate.....		30	15			20
Sodium tripolyphosphate.....				20	20	
Sodium nitrilotriacetate.....		20	15	20	15	10

¹ Pregelatinized.

² The starch hydrolysate product of the similarly designated method of Part One of Examples 14–19.

³ Nonylphenol condensed with about 10 moles of ethylene oxide.

⁴ 3-(N,N-dimethyl-N-hexadecylammonio)-propane.

Each of the compositions of Examples 22–28 exhibit excellent detergency.

EXAMPLE 29

When 85 parts each of the built detergent compositions of Examples 21–28 are mixed with 15 parts water and placed in a Wenger cooking extruder, and the mixture is heated to a temperature of about 280° F. and extruded through a 1/16 inch nozzle opening, the extruded products are puffed ribbons. The extruded ribbons after air drying are ground to form excellent granular detergent products.

In the process of Example 29, the starch derivatives need not be pregelatinized before mixing, since the starch derivatives are gelatinized at the temperatures involved.

All percentages and parts herein are based on weight.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification, and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as fall within the scope of the invention.

What is claimed is:

1. A process for forming detergent granules that are free-flowing and characterized by reduced moisture pick-up, comprising adding water to a detergent composition consisting of from about 10% to about 90% detergent surfactant selected from the group consisting of anionic, non-

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ionic, zwitterionic, ampholytic detergent surfactant and mixtures thereof, and from about 10% to about 90% starch hydrolysates having a D.E. of from about 2 to about 35 to form a pumpable plastic composition;

heating said plastic composition to a temperature of from about 240° F. to 400° F. in a cooking extruder; extruding said heated composition to the atmosphere; and breaking said extruded composition into granules.

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15 U.S. Cl. X.R.

252—89, 132, 135, 370, 539, Digest 2; 264—176