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DETERGENT COMPOSITIONS AND METHODS FOR MAKING SAME

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ABSTRACT OF THE DISCLOSURE

The present invention relates to new detergent compositions and methods for preparing such compositions and more particularly to new detergent compositions in extruded form and methods for producing same.

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From the commercial advent of synthetic detergent materials about 25 years ago as a replacement for soap products and the inexorable advance since then to be substantial total elimination of soap from the laundry cleaning market, and particularly the household market, there has been one predominating technique, particularly in the latter half of this quarter of a century of progress, for producing commercially acceptable product and that is the one of spray drying.

For a single substance spray drying may be an advantage in volume, output and in being able to produce a low density product but this technique has proven particularly desirable with present formulations which contain a multitude of components, e.g. 2 to 20 or more since uniformity or homogeneity of the product is a consequence thereof. Generally the technique involves thoroughly mixing all of the stable and compatible components with sufficient water to form a slurry and to then permitt he spraying into a heated tower usually with high pressure pumps at the top of the tower where one or more spray nozzles reduce the slurry into small fluid droplets which are countercurrently contacted by hot air to dry them; the temperature of the hot air is usually in the range of 250° C. to 350° C. and the amount of water removed usually ranges from 35% to 50% of the total slurry input.

Costwise, spray drying requires a very large capital investment and in view of the large volumes of water to be removed, operating costs may be high although offset by the high output capacity of the towers. In addition, spray drying generally produces, as pointed out above, a low density "bead" which is hollow in nature and consequently is relatively fast dissolving.

It is, at once, evident that spray drying cannot be used with materials which cannot withstand the tower temperature or the high water levels of the slurry to be sprayed. Thus such conventional additives as sodium perborate, enzymes, nonionics, etc. are not feasibly used but most generally be post-added to the spray dried product. Other heat and water sensitive products include certain antioxidants, bleaches, brighteners, bactericides and the like. Many materials, while not decomposed at tower temperatures, cannot be used because of volatility characteristics leading to "pluming" in the tower and losses of such materials. An example of this are some of the ethoxylated hydrophobes (nonionics).

It has now been discovered that detergent compositions may be formulated generally similar to complete, spray-dried detergent compositions in a single, expeditious and low cost manner having all of the advantages of spray dried products, none of the disadvantages and, in fact, are characterized by improvement in the properties of the

spray dried products which are considered a plus for the spray dried form.

The detergent compositions of the present invention are extruded products which are produced by a careful regulation and control of several parameters hereinafter discussed.

The general technique of the present invention involves mixing all the components, in adjusted amounts and relationships, of the final desired composition at their desired level so that when the admixture is worked, as hereinafter described, it is sufficiently "doughy" or plastic to be in suitable form for extrusion in the form of, generally, cylindrical rods needles or "spaghetti." Working may be effected by roll milling followed by extrusion in (1) a conventional soap plodder with the proper extrusion head, (2) a special extruder e.g. Elanco models EXD–60; EXDC–100; EX–130 and EXD–180, or its equivalent, or (3) in a Buhler extruder. In all cases roll milling first, while desirable, is not generally essential.

As pointed out above the components are selected and adjusted so that they may be extruded when "worked", but after extrusion, the spaghetti is a solid, non-tacky product at room temperature and requires no further treatment i.e. water removal, etc. In essence the total composition proceeds from mixing of the component to final packaging without any change in the make-up thereof and without removing any volatiles such as water and the like.

Since much less water is used in the present process as contrasted with spray drying techniques, and it is therefore not necessary to remove water as in spray drying, water sensitive and heat sensitive materials can obviously be incorporated directly into the detergent composition and processed to final form without any detrimental effects thereon. While elevated temperatures are not essential to the operation of the present process it may be desirable to employ temperatures in excess of room temperature e.g. up to 80–100° C. to obtain proper working properties of the detergent mass for extrusion purposes.

During working, as outlined above, heat is usually developed due to frictional forces present as well as hydration of builder salts (i.e. those which will hydrate when present e.g. anhydrous sodium tripolyphosphate, anhydrous sodium carbonate and the like). Such moderate amounts of heat are preferred when necessary for getting the proper consistency of the detergent mass for the extruding step: cooling may be resorted to in order to obtain proper rheological properties if too much heat is developed in the working step.

From the description of the general processing features of the present invention it is clear that there are many parameters to be considered and which may be varied to give optimum performance in the process but within the frame-work of these parameters it is essential that they also be selected so as to yield an extruded product which is characterized by certain specific physical properties. These properties relate to the physical dimensions of the spaghetti, its sheer and tensile strength and its solubility in water.

In order to obtain not only a useful product but an outstanding one as well it is necessary that the spaghetti have an average length of from about 3 to about 10 mm. with 95% thereof within the limits of 0.5 to 20 mm.; an average diameter within the limit of about 0.2 to 2.0 mm. with 0.4 to 0.8 mm. preferred and a bulk density within the range of about 0.3 to 0.8 g./cc.^{3}. The water solubility of the product should be such that the insolubles remaining after 8 grams of product are added to 400 ml. of water at 200 p.p.m. hardness and stirred for three minutes at 400 r.p.m. with a propeller mixer should be less than about 5% at 25° C. and less than about 2%

at 60° C. The amount of insoluble material is determined by filtering the liquid through a #325 wire net and drying the material retained on the screen in an oven at 60° C. for 24 hours. The percent of insolubles so measured is termed "Insolubility Factor." Finally the sheer and tensile strengths should be such that when a length of spaghetti is rested upon two elevated support 12.0 mm. apart it requires a weight of at least 1 gram suspended from the midpoint of said 12 mm. span to break the spaghetti. The number of grams required for breakage is termed "Strength Factor." This is conducted at 20° C. (room temperature).

Since the processes of the present invention are adapted to permit the formulation of all classes of solid detergent compositions i.e. built and unbuilt, with any and all conventional adjuvants, the usual components of the compositions of the present invention include (1) 2–90%, preferably 5–60% and most preferably 8–40% by weight of any of the detergent compound presently known i.e. anionic nonionic, cationic, ampholytic and zwitterionic, alone or in admixture in any compatible manner, with (2) 0–90%, preferably 10–80%, most preferably 20–50% by weight of any inorganic or organic builder or filler salt where desired, but generally preferred, with further (3) any other additives such as anti-redeposition agents (0.05–10%), bleaching agents (0.1–5%), germicides (0.01–2%), enzymes (0.001–5%), anti-oxidants (0.001–5%), brighteners (0.001–2%) foam boosters (0.1–10%), foam suppressors (0.1–15%), hydrotropic agents (0.1–5%), etc.

The anionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and an anionic solubilizing group. Typical examples of anionic solubilizing groups are sulfonate, sulfate, carboxylates, phosphonate, and phosphate. Examples of suitable anionic detergents which fall within the scope of the invention include the soaps, such as the water-soluble salts of higher fatty acids or resin acids, such as may be derived from fats, oils and waxes of animal, vegetable origin, e.g. the sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and the sulfated and sulfonated synthetic detergents, particularly those having about 8 to 26, and preferably about 12 to 22, carbon atoms to the molecule.

As examples of suitable synthetic anionic detergents there may be cited the higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the alkyl group in a straight or branched chain, e.g., the sodium salts of higher alkyl benzene sulfonates or of the higher alkyl toluene, xylene and phenol sulfonates; alkyl naphthalene sulfonate, ammonium diamyl naphthalene sulfonate, and sodium dinonyl naphthalene sulfonate. In one preferred type of composition there is used a linear alkyl benzene sulfonate having a high content of 3- (or higher) phenyl isomers and a correspondingly low content (well below 50%) of 2- (or lower) phenyl isomers; in other terminology, the benzene ring is preferably attached in large part at the 3 or higher (e.g., 4, 5, 6 or 7) position or the alkyl group and the content of isomers in which the benzene ring is attached at the 2 or 1 position is correspondingly low. Particularly preferred materials are set forth in U.S. Pat. 3,320,174, May 16, 1967 of J. Rubinfeld.

Other anionic detergents are the olefin sulfonates including long chain alkene sulfonates, long chain hydroxyalkane sulfonate or mixtures of alkenesulfonates and hydroxylalkanesulfonates. These olefin sulfonate detergents may be prepared, in known manner, by the reaction of SO_3 with long chain olefins (of 8–25, preferably 12–21, carbon atoms) of the formula

$$RCH=CHR_1,$$

where R is alkyl and R_1 is alkyl or hydrogen, to produce a mixture of sultones and alkenesulfonic acids, which mixture is then treated to convert the sultones to sulfonates. Examples of other sulfate or sulfonate detergents are paraffin sulfonates having, for example, about 10–20, preferably about 15–20, carbon atoms such as the primary paraffin sulfonates made by reacting long chain alpha olefins and bisulfites (e.g. sodium bisulfite) or paraffin sulfonates having the sulfonate groups distributed along the paraffin chain such as the products made by reacting a long chain paraffin with sulfur dioxide and oxygen under ultra-violet light followed by neutralization with NaOH or other suitable base (as in U.S. Pats. 2,503,280; 2,507,088; 3,260,741; 3,372,188 and German Pat. 735,096); sulfates of higher alcohols; salts of α-sulfofatty esters (e.g. of about 10 to 20 carbon atoms, such as methyl α-sulfomyristate or α-sulfotallowate).

Examples of sulfates of higher alcohols are sodium lauryl sulfate, sodium tallow alcohol sulfate, Turkey Red Oil or other sulfated oils, or sulfates of mono- or di-glycerides of fatty acids (e.g. stearic monoglyceride monosulfate), alkyl poly (ethenoxy) other sulfates such as the sulfates of the condensation products of ethylene oxide and lauryl alcohol (usually having 1 to 5 ethenoxy groups per molecule); lauryl or other higher alkyl glyceryl ether sulfonates; aromatic poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and nonyl phenol (usually having 1 to 6 oxyethylene groups per molecule).

The suitable anionic detergents include also the acyl sarcosinates (e.g. sodium lauroylsarcosinate) the acyl esters (e.g. oleic acid ester) of isethionates, and the acyl N-methyl taurides (e.g. potassium N-methyl lauroyl- or oleyl tauride).

The most highly preferred water soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono-, di and triethanolamine), alkali metal (such as calcium and magnesium) salts of the higher alkyl benzene sulfonates, olefin sulfonates, the higher alkyl sulfates, and the fatty acid monoglyceride sulfates. The particular salt will be suitably selected depending upon the particular formulation and the proportions therein.

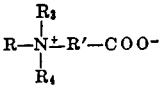
Nonionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and a hydrophilic group which is a reaction product of a solubilizing group such as carboxylate, hydroxyl, amido or amino with ethylene oxide or with the polyhydration product thereof, polyethylene glycol.

As examples of nonionic surface active agents which may be used there may be noted the condensation products of alkyl (C_6 to C_{20} straight or branched chain) phenols with ethylene oxide (3–100 moles), e.g., the reaction product of isooctyl phenol with about 6 to 30 ethylene oxide units; nonyl phenol with 9 moles ethylene oxide; dodecyl phenol with 11 moles ethylene oxide; condensation products of alkyl (C_6 to C_{20}) thiophenols with 3 to 100 ethylene oxide units; condensation products of higher (C_8 to C_{30} fatty alcohols such as tridecyl alcohol with ethylene oxide (3–100 moles) e.g. C_{16}–C_{18} alcohol plus 11 or 50 ethylene oxide; ethylene oxide addends of monoesters of hexahydric alcohols and inner ethers thereof with higher (C_8–C_{30}) fatty acids such as sorbitan monolaurate, sorbitol mono-oleate and mannitan monopalmitate, and the condensation products of polypropylene glycol (e.g. MW=1500–1800) with ethylene oxide (3–100 moles).

Examples of suitable amphoteric detergents are those containing both an anionic and a cationic group and a hydrophobic organic group, which is advantageously a higher aliphatic radical, e.g. of 10–20 carbon atoms. Among those are the N-long chain alkyl aminocarboxylic acids (e.g. of the formula

$$R-\underset{\displaystyle R_2}{\overset{|}{N}}-R'-COOM)$$

the N-long chain alkyl iminodicarboxylic acids (e.g. of the formula $RN(R'COOM)_2$) and the N-long chain alkyl betaines (e.g. of the formula



where R is a long chain alkyl group, e.g. of about 10–20 carbons, R' is a divalent radical joining the amino and carboxyl portions of an amino acid (e.g. an alkylene radical of 1–4 carbon atoms), N is hydrogen or a salt-forming metal, R_2 is a hydrogen or another monovalnet substitutent (e.g. methyl or other lower alkyl), and R_3 and R_4 are monovalent substitutents joined to the nitrogen by carbon-to-nitrogen bonds (e.g. methyl or other lower alkyl substituents). Examples of specific amphoteric detergents are N-alkyl-beta-aminopropionic acid; N-alkyl-beta-iminodipropionic acid, and N-alkyl, N,N-dimethyl glycine; the alkyl group may be, for example, that derived from coco fatty alcohol, lauryl alcohol, myristyl alcohol (or a laurylmyristyl mixture), hydrogenated tallow alcohol, cetyl, stearyl, or blends of such alcohols. The substituted aminopropionic and iminodipropionic acids are often supplied in the sodium or other salt forms, which may likewise be used in the practice of this invention. Examples of other amphoteric detergents are the fatty imidazolines such as those made by reacting a long chain fatty acid (e.g. of 10 to 20 carbon atoms) with diethylene triamine and monohalocarboxylic acids having 2 to 6 carbon atoms, e.g. 1-coco - 5-hydroxyethylene-5-carboxymethylimidazoline; betaines containing a sulfonic group instead of the carboxylic group betaines in which the long chain substitutent is joined to the carboxylic group without an intervening nitrogen atom, e.g. inner salts of 2-trimethylamino fatty acids such as 2-trimethylaminolauric acid, and compounds of any of the previously mentioned types but in which the nitrogen atoms is replaced by phosphorus.

As builder salts one may use phosphates and particularly condensed phosphates (e.g. pyrophosphates or tripolyphosphates), silicates, borates and carbonates (including bicarbonates), as well as organic builders such as salts of nitrilotriacetic acid, ethylene diamine tetracetic acid, glycollic acid, citric acid etc. Sodium and potasium salts are preferred. Specific examples are sodium tripolyphosphate, potassium pyrophosphate, sodium hexametaphosphate, sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium tetraborate, sodium silicate, salts (e.g. Na salt) of methylene diphosphonic acid, disodium diglycollate, sodium citrate, trisodium nitrilotriacetate, or mixtures of such builders, including mixtures of pentasodium tripolyphosphate and trisodium nitrilo-triacetate in a ratio, of these two builders, of 1:10 to 10:1, e.g. 1:1. Other builders include the organic polyelectrolytes such as methyl vinyl ether-maleic anhydride interpolymers and their hydrolyzed acids and salts (e.g. sodium, potassium, ammonium and amine).

Various other materials may be present in the granular washing products. Thus, materials such as the higher fatty acid amides may be added to improve detergency and modify the foaming properties in a desirable manner. Examples thereof 2,6-di-tert-butylphenol, or other phenolic antioxidant materials (e.g. in amounts in the range of about 0.001% to 5%), coloring agents, bleaching agents and other additives.

As indicated, the washing product may contain a water-soluble peroxy bleaching compound, such as sodium perborate (e.g. sodium perborate tetrahydrate or monohydrate), sodium percarbonate, etc.

The proportions of peroxy compound in the washing product is preferably such as to provide in the range of about 2 to 3% active oxygen based on the weight of washing powder. Typically the proportion of sodium perborate tetrahydrate is in the range of about 10 to 50% based on the total weight of the washing product with 25% being an often used amount.

Enzyme materials which can be used include any proteolytic, amyltic, lipolytic, etc. enzyme. Of particularly prominent use are the proteolytic enzymes which include pepsin, trypsin, chymotrypsin, papain, bromelin, colleginase, keratinase, carboxylase, amino peptidase, elastase, substilisia and aspergillo-pepidase A and B. Preferred enzymes are subtilisin enzymes manufcatured and cultivated from special strains of spore forming bacteria, particularly *Bacillus subtilis.*

Proteolyytic enzymes such as Alcalase, Maxatase, Protease AP, Protease ATP 40, Protease ATP 120, Protease L–252 and Protease L–423 are among those enzymes derived from strains of spore foaming bacillus, such as *Bacillus subtilis.*

Different proteolytic enzymes have different degrees of effectiveness in aiding in the removal of stains from textiles and linen. Particularly preferred as strain removing enzymes in this invention are subtilisin enzymes.

Metalloproteases which contain divalent ions such as calcium, magnesium or zinc bound to their protein chains are of interest.

Conventional fillers include sodium sulfite and sodium chloride but others, if available, may also be used.

As pointed out above, the essential features of the processes of the present invention include a proper formulation of ingredients to yield a doughy or plastic mass during the working thereof and which permits of the formation therefrom, by extrusion, of threads or spaghetti of a totally formulated detergent composition, the spaghetti having the necessary characteristics of length, diameter, shear and tensile strengths and water solubility described above.

In Italian application 410,48A/69 there are described suitable milling rolls and ribbon-type amalgamator as illustrative of suitable equipment which may be used in the present invention. Other suitable equipment, but not limitative of the types which may be employed, is disclosed in Italian application (IR 184–F) filed of even date herewith and titled "Extruder Output Multiplier." The disclosures of these applications is incorporated herein by reference thereto.

The products of the present invention, in addition to being characterized by the advantageous and superior properties heretoforce described also exhibit outstanding and unexpected superiorities in other areas. Thus it is known that in producing spray dried detergents there is a degradation of the initially added tripolyphosphate (generally to pyrophosphate) and this leads to a decided loss in efficiency of the final product. In the present process no degradation of the tripolyphosphate occurs. In addition, in an enzyme-containing spray dried detergent containing a bleach (e.g. sodium perborate) the stability of the enzyme is poor whereas in the present composition the stability is excellent. Still further, perborate levels remain as high as in spray dried detergents (where it is essential to post add the perboate to prevent serious losses in the processing i.e. in the spray tower); also, most unexpectedly the products of the present invention have better solubility characteristics than spray dried materials. A further notable improvement lies in the better whiteness of the products of this invention when compared to spray dried, similar compositions. Still another great advantage of the process and products of this invention lies in better efficiency of perborate-containing detergent during washing. With spray dried products to which perboate is and must be post added there are losses of active oxygen of 30% or more due to too rapid solution of the perborate. This does not occur with the compositions of the present invention,

The following examples will serve to illustrate the present invention without being deemed limitative thereof. Parts are by weight unless otherwise indicated.

EXAMPLE 1

5 Kilos of sodium perborate tetrahydrate and 8.4 Kilos of anhydrous pentasodium tripolyphosphate, both in the form of a fine powder with no particles over U.S. mesh N. 40, are weighed and added into a soap type amalgamator.

The following materials are also weighed and added: 0.8 Kilos of spray dried linear dodecyl benzene sulphonate (74% AI), 0.12 Kilos of sodium carboxymethyl cellulose, 1.14 Kilos of ethoxylated alcohol [(C_{16}–C_{18}) +50 moles ethylene oxide], 0.06 Kilos of optical dyes. The mixer is started to get a uniform mixture of the powders and then the following materials are added:

2.046 Kilos of tallow soap made in a separate vessel mixing together 0.772 Kilos of tallow fatty acids, 0.248 Kilos of caustic soda (38% Na_2O) and 1.026 Kilos of water. 2.463 Kilos of liquid sodium silicate Na_2O/SiO_2 1:12 (44% solids) are then poured in the amalgamator while mixing.

The resulting product is a paste which is passed over a 3 roll mill and then extruded in a laboratory plodder (the temperature of the circulating water in the barrel ranges from 40 to 55° C. during extrusion. Air to cool the spaghetti to room temperature is continuously blown on the extruder and) equipped with a perforated plate and a wire net (0.55 mm. opening) to obtain a needle shaped, free flowing product. Analysis of the product shows no active oxygen loss during extrusion; the apparent density is 0.52.

EXAMPLE 2

A composition similar to Example 1 is tested on a pilot extruding plant (20 Kilos batch) with the following changes: The spray dried alkyl arly sulfonate in powder form is replaced by 1.6 Kilos of High AI slurry (43% solids) and less water is added in the liquid soap (0.226 Kilos instead of 1.026 Kilos in Example 1). Finally 0.06 Kilos of detergent type perfume are added at the end of the mixing operation. The product is extruded through a perforated sheet with round holes 0.6 mm. diameter placed behind the perforated plate.

EXAMPLE 3

The procedures of Examples 1 and 2 are repeated but 1 Kilo of tripolyphosphate is replaced by 1 Kilo of sodium sulphate to reduce friction in the plodder.

EXAMPLE 4

As in Examples 1 and 2, but 1.40 Kilos of tripolyphosphate are replaced by the same quantity of tetrasodium pyrophosphate to reduce friction in the plodder.

EXAMPLE 5

Examples 1 to 4 are repeated but 5 Kilos of sodium perborate tetrahydrate are replaced by 3.3 Kilos of monohydrate and 2.667 Kilos of sodium sulphate; 7.34 Kilos of TPP are used in the mixer. Analysis of the products of Examples 2 through 5 are given in Tables I and II below.

TABLE I

	Analyzed for—							
	Apparent density		Total weight, percent	P_2O_4, percent	Na_3PO_4, percent	$Na_4P_2O_4$, percent	$Na_5P_3O_{10}$, percent	Perborate tetrahydrate, percent
	Filled	With shakes						
Composition Ex.:								
2	0.50	0.57	24.2	23.9	0.37	2.57	38.61	23.5
3	0.57	0.64	25.3	24.5	0.35	2.02	40.17	25.4
4	0.58	0.64	24.4	23.8	0.35	[1] 9.12	32.40	22.4
5	0.52	0.65	15.3	21.1	0.28	2.18	31.15	23.1
Spray dried product [2]	0.36	0.43	20.0	22.5	0.59	10.5	28.0	24.0

[1] This indicates the added pyrophosphate.
[2] Essentially similar in composition to Examples 2-5 except that part of the tripolyphosphate, part of the nonionic and all of the perborate are post added to the balance of the composition which has been spray dried.

NOTE.—In the above examples the amount of perborate added (nominal) is 24-25%.

TABLE II

	Length distribution, percent in the range			
	0-3 mm.	3-6 mm.	6-9 mm.	9-12 mm.
Composition Ex.:				
2	11	57	30	2
3	50	49	1	0
4	63	34	3	0
5	7	65	28	0

From Table I is it clear that a substantial amount of the tripolyphosphate in the spray dried product degrades to pyrophosphate and this does not occur with the compositions of the present invention.

To the products of Examples 2, 3, 4 and 5 there is added 2.8% of an enzyme-containing spaghetti containing 25% alcalase Novo 1.5 Au/g. using magnesium lauryl sulfate as a binder and prepared as described in Italian application 55,270A/70 filed Dec. 9, 1970. The enzyme content (nominal) of the detergent is 0.700% of Alcalase Novo 1.5 Au/g. The perborate content is 26%. Accelerated aging tests are carried out on such products and a spray dried product of the same compositions to which the enzyme, perborate and part of the tripolyphosphate and non-ionic are post added. The tests are conducted in non-barrier cartons for 4 weeks at 43° C. The results are set forth in Table III below along with results obtained using non-enzyme product.

TABLE III

	With enzyme		Without enzyme, percent perborate
	Percent perborate	Percent enzyme	
Composition Ex.:			
2	22.7	0.53	22.8
3	24.0	0.51	24.6
4	22.7	0.52	23.1
5	21.6	0.58	22.1
Spray dried	22.6	0.28	22.5

The above data demonstrate that the perborate and enzyme stability is excellent in the products of this invention and that there is excessive and severe losses in enzyme in the spray dried product.

EXAMPLE 6

With a procedure similar to the one used in Example 1, the following composition is prepared:

The following materials are weighed and added in a mixer (soap type amalgamator):

	Kilos
Moisturized pentasodium tripolyphosphate	2.715
Spray dried alkyl aryl sulfonate (74% AI) (of Ex. 7)	0.718
Sodium nitrilo triacetate 99.5%	0.600
Sodium sulphate anhydrous	0.420
Optical dyes	0.016
Sodium carboxymethyl cellulose	0.044
Bacteriostat (Temasept IV)—Tribromosalicylanilide	0.003

The following liquid ingredients are added in the mixer previously strated:

Tallow soap made by mixing together:

Tallow fatty acids	Kilos	0.110
Caustic soda 38% Na_2O	do	0.036
Water	do	0.300
Total		0.446
Sodium silicate (1:2), 44% solids		0.839
Liquid nonionic (Empilan NP 9) ethoxylated nonylphenol with 9.5 moles condensed ethylene oxide)		0.181
Perfume		0.018

The product is processed as in the former example, with a 0.55 mm. wire net on the plodder and a needle shaped free flowing material is obtained.

EXAMPLE 6A

Solubility of spaghetti detergent in comparison with spray dried detergent.

The following test is used:

8 grams of product are dissolved in 400 ml. of water at 200 p.p.m. hardness and mixed for 3 minutes at 400 r.p.m. with a propeller mixer. The liquid is filtered through a #325 wire net and the undissolved product dried in an oven at 60° C. for 24 hours.

Results:

	Percent undissolved in water (200 p.p.m.)	
	25° C.	40° C.
Spaghetti as in Example 2	3.4–3.8	1.4–1.5
Sprayed dried composition of Example 2	6.9	5.4–5.6
Competitive Product 1	4.5–5.1	2.5–2.6
Competitive Product 2	7.9–8.3	4.8–5.4

Estimate of the product remaining in the dosers of washing machines:

The product is recovered from the machine dosers, dried at 60° C. in an oven for 24 hours and the percentage calculated. The results are set forth in Table IV.

EXAMPLE 7

With a procedure similar to the former examples the following composition is prepared:

	Kilos
Pentasodium tripolyphosphate (moisturized type) fine powder	2.715
Sodium perborate tetrahydrate (fine powder)	0.600
Sodium sulphate anhydrous (fine powder)	0.471
Sodium carboxymethyl cellulose (detergent grade)	0.044
Optical dyes	0.016
Bacteriostat (Temaspet IV)	0.003

All these materials in powder form are weighed and charged into a mixer.

The following blend of liquid ingredients is prepared in a separate vessel at a temperature of 70° C., mixing with an open turbine propeller and with the listed order of addition:

	Kilos
(1) Tallow fatty acids	0.110
(2) Dodecylbenzenesulfonic acid	0.600
(3) Water	0.037
(4) C_9 alkyl phenol EO 9.5:1 (Nonionic)	0.181
(5) Caustic soda (38% Na_2O)	0.203
(6) Sodium silicate 1:2 (44% solids)	1.002

The sodium silicate is added after the neutralization of the acids.

The resulting product is poured into the amalgamator over the previously charged powder under mixing.

After a few minutes a paste is formed and 0.018 Kilos of detergent grade perfume is added.

The product is extruded in the manner described above through a 0.55 wire net, cooling the extrudate with air at room temperature.

EXAMPLE 8

A composition similar to example 7 is prepared except that the Alkyl aryl sulphonate is added in the form of spray dried powder instead of the liquid acid form.

The extrusion is made first in the usual way (flat perforated plate and wire net 0.55 mm.) obtaining a density of 0.49 filled and 0.55 tamped. A second experiment is made using a perforated cylinder adapted to the plodder by means of a flange, containing a wire net (05.5 mm.) in contact with the inner surface; a small perforated pipe is fixed in the cylinder for compressed air introduction. The air during extrusion has a pressure of 8 Kilos/sq. cm. and the resulting product has a density of 0.46 filled, 0.51 tamped.

EXAMPLE 9

The following composition of dishwashing high suds granular deteregnt is prepared with a similar procedure, referring to the former examples.

TABLE IV

		Machine type									
	Water pressure, kg./sq. cm.	Candy 88		Castor 685		Indesit bio		Rex G 554		Castor stice	
Detergent type		P	M	P	M	P	M	P	M	P	M
Extruded detergent (example 2)	0.3	6.8	13.4	Nil	16.7	D	Nil	Nil	Nil	D	8.9
	0.4	Nil	15.7	Nil	Nil					D	Nil
Spray dried detergent	0.3	8.3	18.0	Nil	12.3		Nil	Nil	5.9		18.9
	0.4	Nil	19.5	Nil	Nil			Nil	Nil		16.1

NOTE.—P=Prewash cycle; M=Main wash cycle; D=Direct feeding or machine drum.

In a tiltable type amalgamator (to avoid leaking of liquids) the following materials are weighed and charged with the listed order of addition:

	Kilos
(1) Tap water	0.600
(2) Sodium carbonate	0.600
The mixer is running during addition of carbonate.	
(3) Doceylbenzenesulphonic acid	2.160
After the mass has reacted the following are added with the mixer running:	
(4) Sodium sulphate anhydrous	2.334
(5) Tetrasodium pyrophosphate (fine powder)	0.300
(6) Perfume	0.006

the pH is adjusted to 7 with small additional quantities of sodium carbonate and the resulting paste milled through a 3 roll mill and extruded throuugh a 0.55 mm. wire net.

The granular product analyzes 9.4% moisture 35.2% active ingredient and has a density of 0.40 filled, 0.50 tamped.

EXAMPLE 10

In the following example a low sudsing granular detergent is prepared with similar procedure referring to the former examples.

A phosphoric ester active agent is used to add a softer feel to the washed clothes:

The order of addition is as listed (All solids are fine powders.):

	Kilos
(1) Pentasodium tripolyphosphate	4.000
(2) Sodium perborate monohydrate	1.468
(3) Sodium sulphate anhydrous	0.627
(4) Sodium chloride	0.500
(5) Sodium carboxymethyl cellulose	0.060
(6) Optical dyes	0.030

The following slurry is prepared in a separate vessel following the listed order of addition:

	Kilos
(A) Tallow fatty acids	0.383
(B) Berol phosphoric ester TVM 729 (ethoxylated nonyl phenol phosphated to give 60% diester and 40% monoester)	0.433
(C) Caustic soda, 38% Na_2O	0.282
(D) Tap water	0.500
(E) Sodium dodecyl (linear) benzene sulphonate (50% solids)	0.568
(F) Sodium silicate 1:2 (44% solids)	0.900
(G) Ethoxylated nonyl phenol (Empilan NP 9)	0.030

The slurry so prepared, at a temperature of about 75° C., is added to the previously weighed powders in an amalgamator, while running.

A paste like white material results to which 0.020 Kilos of detergent grade perfume are added.

The product is milled and extruded as described above.

The product has a moisture of 15%.

EXAMPLE 11

The following low phosphate composition is prepared. (All solids are fine powders.):

	Kilos
Pentasodium tripolyphosphate (moisturized type)	1.615
Sodium sulphate anhydrous	4.510
Sodium nitrilo triacetate (99.5% purity)	1.013
Sodium carboxymethyl cellulose (detergent grade)	0.070
Optical dyes	0.030

All these materials are weighed and added into a soap type amalgamator.

The mixer is started and a liquid soap at 80° C. is added. The composition of soap is:

	Kilos
Distilled tallow fatty acids	0.534
Caustic soda (38% Na_2O)	0.200
Tap water	1.375

The following materials are also charged into the amalgamator:

	Kilos
Sodium Alkyl aryl sulphonate (from linear dodecyl benzene) (51.5 active ingredients)	0.650
Sodium silicate 1:2 (44% solids)	0.656
Ethoxylated nonyl phenol (9.5 EO)	0.056

The mixer is always running while adding the ingredients. After 5 minutes a uniform paste like material is formed to which 0.025 Kilos of detergent grade perfume is added.

The product is then milled and extruded as in the previous examples. The moisture of finished product is 10.5%.

EXAMPLE 12

Order of addition as listed:	Kilos
(1) Pentasodium tripolyphosphate (moisturized type)	22.650
(2) Sodium perborate tetrahydrate	13.020
(3) Sodium chloride	3.000
(4) Sodium carboxymethyl cellulose	0.360
(5) Sodium dodecyl benzene sulphonate (from linear alkyl benzene) (51.5% active ingredients)	4.800
(6) Tallow wet soap (32% moisture)	4.410
(7) Sodium silicate 1:2 (48% solids)	7.332
(8) Tap water	0.540
(9) Ethoxylated C_{16}–C_{18} Alcohol 50 EO (in a liquid state 70° C.)	3.420
(10) Optical dyes	0.162
(11) Ethylene diammin sodium triacetate (ETA)	0.120
(12) Antioxidant (BHT)	0.002
(13) Ultramarine Blue	0.003
(14) Detergent perfume	0.180

The mixture is prepared in a Lodige mixer, milled through a 3 roll mill and extruded through a pilot plant extruder equipped with the extruder multiplier subject of the invention record No. 11 (184–F) of Feb. 27, 1970 filed of even date herewith.

A wire net of 0.60 mm. is placed in the cylinder and a small screw is rotating inside it. The product is cooled at room temperature by means of air blowing at the extruder end. The finished product analytical characteristics are:

	Percent
Moisture	22.5
Active ingredient	3.7
P_2O_5	21.4
Nonionic	5.6
Active oxygen	2.0

These characteristics are comparable with those of a spray dried, post added detergent.

The bulk density is 0.52 filled, 0.60 tamped. The product is free flowing, has a nice appearance and is free from any dust and dissolves faster than the conventional spray dried product.

EXAMPLE 13

Examples 1 and 2 are repeated replacing the dodecyl benzene sulphonate with the following active ingredients in the same amounts.

(A) C_{16}-α-olefin sulphonate, sodium salt
(B) C_{14}-α-olefin sulphonate, sodium salt
(C) tetradecane sulphonate, sodium salt
(D) hexadecane sulphonate, sodium salt
(E) 1:1 weight ratio of sodium dodecyl benzene sulphonate and sodium tetradecane sulphonate
(F) 4:1 weight ratio of sodium linear tridecyl benzene sulphonate and sodium tallow alcohol sulfate.

Excellent results are obtained.

While the invention has been illustrated with respect to certain ingredients and conditions, it will be clear that all variations and equivalent materials and conditions as taught herein may be employed. Further, the use of the detergent products of this invention are not to be limited specifically to what is described. Thus, if one desires the products which are dry, non-tacky, strong, dust-free, quickly soluble and stable may be employed to produce excellent spheronized particles as described in Italian patent application No. 55,581A/70 filed Dec. 22, 1970.

I claim:

1. A process for producing a detergent composition containing 2 to 90% of a detergent selected from the group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic detergents and from 10 to 80% of a detergent builder salt which comprises mixing said components in the presence of sufficient water and at a temperature from room temperature to 100° C. to produce a doughy mass capable of being extruded to form dry, non-tacky spaghetti-like particles at ambient temperatures without removing any significant volatiles during the entire operation, extruding said doughy mass in the form of spaghetti-like particles and bring said particles to ambient temperature, said particles having an average length of from about 3 to about 10 mm. with 95 weight percent thereof within the limits of from 0.5 to 20 mm., an average diameter of from about 0.2 to 2.0 mm., a bulk density of from 0.3 to 0.8 g./cc.^{3} and insolubility factor at 25° C. of less than 5 and a strength factor of at least 1.

2. A process as defined in claim 1, wherein the anionic surface active agent is an alkyl benzene sulfonate, and wherein the detergent builder salt is a water soluble phosphate, carbonate, silicate, borate, citrate, glycollate or organic polymeric electrolyte.

3. A process as defined in claim 2 wherein the detergent composition includes a water soluble fatty acid soap and 10 to 50% of a peroxygen compound.

4. A product produced by the process of claim 1.

5. A product produced by the process of claim 3.

References Cited

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MAYER WEINBLATT, Primary Examiner

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