PATENT SPECIFICATION

(11) 1 591 516

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(21) Application No. 50120/77 (22) Filed 1 Dec. 1977 (19)

(31) Convention Application No. 747001 (32) Filed 2 Dec. 1976 in

(33) United States of America (US)

(44) Complete Specification Published 24 Jun. 1981

(51) INT. CL.[3] C11D 3/04
(C11D 3/04 1/66 3/065)

(52) Index at Acceptance
C5D 6A5B 6A5C 6A5D2 6A5E 6B12B1
6B12G2A 6B12N1 6C6 6D

(54) DETERGENT COMPOSITIONS

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process for manufacturing low density detergent builder base particles to which a detergent may be added to form a low density, particulate, built synthetic organic detergent composition.

The invention is based on the discovery that if a small proportion of an organic hydrotropic salt is included in a crutcher mix before spray drying a substantially inorganic particulate base composition, the presence of the hydrotrope in the crutcher mix results in production of substantially lower density base. The base particles can subsequently be coated with a nonionic detergent to form a low density, particulate, built nonionic detergent composition. Also within the invention are a method for manufacturing such low density base particles, and particulate base and particulate built synthetic organic detergent compositions which may be made by such methods.

Recently, built particulate synthetic organic detergents based on nonionic detergents have been found to possess various advantages over the previously conventional heavy duty, built, particulate anionic synthetic organic detergents. However, when manufacture of the built nonionic detergent compositions was undertaken by methods previously used for producing anionic detergent counterparts, such as by spray drying the final composition from a crutcher mix, various problems were encountered. The most objectionable of these was fuming of the nonionic detergent during the spray drying process, causing objectionable smoke from the spray drying plant and resulting in the loss of the detergent. In addition to being objectionable from the environmental standpoint the process is more costly and results in the production of detergent composition particles of widely varying active ingredient (nonionic detergent) content, depending on spray tower conditions. Accordingly, post-addition (i.e. addition after spray drying) of most or all of the nonionic detergent has been suggested and commercial products have been made by such method. See U.S. patents 3,838,072; 3,849,327; 3,886,098; and 3,971,726; and German Offenlegungsschrift 2,514,677.

Although post-addition of the nonionic detergent, usually by spraying a melt thereof onto the surfaces of moving particles of a base composition, which is usually substantially inorganic and constitutes the remainder of the detergent composition or most of the remainder thereof, results in a useful product, generally such product will be of a higher bulk density than that previously produced when anionic detergents (including soaps) were present in the crutcher mix. In some instances the higher density particles are acceptable and even desirable but in many cases it is desirable to produce low bulk density products, such as those to which the consumer has previously been accustomed, the bulk densities of which are usually in the 0.3 to 0.5 g/cc range. It has been found that when a substantially inorganic crutcher mix is spray dried the beads produced thereby, after nonionic detergent addition, will be of a higher density than desired, such densities often being in the 0.55 to 0.75 g/cc range. When nonionic detergent is post-sprayed or otherwise coated onto the base composition particles the densities thereof are increased slightly or sometimes may remain about the same. Thus, so as to be able to produce a commercial built heavy duty nonionic detergent product, efforts have been made to decrease the bulk density of the spray dried beads of the base composition and to make a low density particulate detergent from such base particles.

The use of soap and other anionic detergents, in small quantities, as constituents of an essentially inorganic crutch mix has been found to lower the bulk density of the dried particles resulting from spray drying. Such effects are described in U.S. patent 3,971,726 and in the German Offenlegungsschrift previously mentioned. However, the use of such detersive products, even in comparatively small proportions, may promote foaming, which is often undesirable for particular detergent compositions. Furthermore, with the use of small quantities of anionic detergents, as described in the German Offenlegungsschrift, certain specific operating conditions may have to be maintained in the spray tower and in some cases only particular compositions will be capable of being produced in the desired low bulk density range. Such undesirable properties in the product and such restrictions on the compositions and methods employed may be obviated by the present processes and satisfactory compositions may be made utilizing them.

According to one aspect of the present invention a process for manufacturing a low density substantially inorganic particulate base composition useful for conversion to a built synthetic organic detergent composition by addition of a nonionic detergent thereto comprises mixing together a plurality of components of a crutcher mix, including inorganic builder(s), water-soluble organic hydrotropic salt(s) and water in such proportions that when subsequently dried the water-soluble organic hydrotropic salt(s) present significantly-reduce(s) the density of the product, and drying the mix.

According to another aspect of the invention such a base composition *per se* comprises from 22% to 44% of sodium tripolyphosphate, from 3.3% to 16.7% of sodium carbonate, from 5.6% to 16.7% of sodium silicate of Na_2O:SiO_2 ratio in the range from 1:1.6 to 1:3, from 1.1% to 3.3% of sodium toluene sulphonate and/or sodium xylene sulphate, 0 to 5.6% of borax, from 22% to 56% of sodium sulphate and from 5.6% to 13.3% of water.

A process for manufacturing such a detergent composition comprises applying onto the surfaces of particles of a particulate base composition as aforesaid a detersive proportion of nonionic detergent.

Thus, a process for manufacturing a low density, particulate, built synthetic organic detergent composition may comprise mixing together a plurality of components of a crutcher mix, including inorganic builder(s) such as sodium tripolyphosphate, sodium silicate and sodium carbonate, often with inorganic filler salt(s) such as sodium sulphate, water-soluble organic hydrotropic salt(s), such as sodium toluene sulphate and/or sodium xylene sulphonate, and water, in such proportions that when subsequently dried the water-soluble organic hydrotropic salt(s), usually present to the extent of from 0.2% to 5% in the crutcher mix and preferably from 1.2% to 2% in the final product, significantly reduce(s) the density of the product (to 0.25 or 0.3 to 0.45 or 0.5 g/cc [0.25 to 0.45 g/cc in the base composition particles]), drying the mix, preferably by spray drying under normal conditions, and applying to the surfaces of particles of the dried mix, as by spraying, a detersive proportion, usually from 5% to 17%, preferably from 7% to 15%, of nonionic detergent, preferably a fatty alcohol polyethylene oxide condensate.

The base detergent composition, sometimes referred to as the carrier composition, will usually be composed substantially of inorganic materials, primarily inorganic builder(s) and preferably also inorganic filler salt(s). However, it may also contain other desirable constituents of the final detergent composition, except the nonionic detergent, which are sufficiently heat stable to withstand a drying operation, such as conventional spray drying. Preferably, any anti-redeposition agent, such as sodium carboxymethyl cellulose, and any quantity of sodium silicate in excess of about 15%, preferably 10%, on a base composition basis, will be post-added, before, after or with the nonionic detergent, preferably as particulate solids. If desired, flow promoting clays such as that sold under the trademark SATINTONE, may also be post-added but use thereof is not normally needed for the manufacture of a sufficiently free flowing, non-tacky and non-caking product. Colorants, perfumes, fluorescent brighteners, fungicides, herbicides and other adjuvants may also be post-added and when sufficiently soluble, may be dispersed or dissolved in the nonionic detergent and applied to the base particles with it, as by spraying.

The builder components of the present compositions are preferably water-soluble polyphosphates, carbonates, silicates, borates, bicarbonates and phosphates, usually as the sodium or potassium salts, e.g., pentasodium tripolyphosphate, tetrapotassium pyrophosphate, sodium carbonate, potassium bicarbonate, sodium silicate (Na_2O:SiO_2=1:2.35), borax and disodium hydrogen phosphate, but it is contemplated that organic builder salts may also be employed, at least in partial replacement of the inorganic builders. Such replacement may also be made with water-insulble builders such as sodium aluminosilicates, preferably zeolites of Types A or X, crystalline or amorphous, various examples of which are disclosed in U.S. patent 2,882,243; Belgian patents 813,581 and 835,351; and British patent specifications Nos. 1,473,201, 1,473,571, 1,473,572 and 1,464,427. Additionally such insoluble builders are described in the textbook *Zeolite Molecular Sieves* by Donald W. Breck, published in 1974 by John Wiley & Sons, specifically being listed in Table 9.6 at pages 747-49 thereof. Of the builders present, normally at least 50% will be water soluble inorganic builder salts. Preferably, this proportion will be at least 80%, more preferably at least 90%, and most preferably 100%. Although it is not essential to incorporate a filler salt in the base beads or in the final detergent composition, generally the presence of such material will be desirable. Among the best of the fillers, contributing particle strength, stability and flowability at relatively low cost, is sodium sulphate, which will usually be all of a major proportion of the filler present, usually being over 50% and preferable over 90% of the filler content. However, other water-soluble and non-deliquescent inorganic salts which are heat stable may also be employed, such as sodium chloride, sometimes found as an impurity in one of the product components, potassium sulphate, sodium bisulphate and potassium chloride.

The hydrotropic salt, which has been found to aid in the manufacture of the low density carrier particles of this invention, may be any such compound which has the property of promoting water solubility of only slightly soluble compounds and of aiding in the production of low density carrier and final product particles, especially when crutcher mixes of a base composition are spray dried at elevated temperatures. The preferred compounds of this type are water-soluble salts of substituted or unsubstituted benzene sulphonic acids, such as the sodium and potassium salts thereof (alkali metal salts), especially the sodium salts. Although alkali metal benzene sulphonates, such as sodium benzene sulphonate, are useful hydrotropes and may be employed in the processes of this invention, it is preferred to have one or more hydrogens of the benzene ring substituted, as by a lower alkyl group of 1 to 4 carbon atoms, preferably 1 or 2 carbon atoms and most preferably one carbon atom (methyl), e.g., sodium toluene sulphonate, sodium xylene sulphonate, potassium toluene sulphonate and corresponding salts of cumene, mesitylene, ethylbenzene and pseudocumene. Usually, the sulphonates are mixtures of isomers, with para- and ortho-configurations normally and preferably dominating, e.g., sodium *p*-methyl benzene sulphonate, sodium *O*,*O*-dimethyl sulphonate, sodium *o*,*p*-dimethyl benzene sulphonate. Also, mixtures of the various different types of hydrotropes may be used, e.g., sodium toluene sulphonate and sodium xylene sulphonate or the corresponding potassium salts.

The nonionic detergents employed are preferably polyethoxylated higher fatty alcohols such as the water-soluble condensation products of 3 to 15 mols of ethylene oxide, preferably 7 to 11 mols, and higher fatty alcohols of 10 to 18 carbon atoms, preferably 12 to 15 carbon atoms. Such nonionic detergents melt or soften sufficiently to be sprayable in droplet form at a temperature below 45°C. A preferred commercial product, which is the condensation product of a higher fatty alcohol mixture of 12 to 15 carbon atoms with about 7 mols of ethylene oxide per mol of fatty alcohol, is sold under the trademark Neodol 25-7, manufactured by Shell Chemical Co (NEODOL is a trade mark). Other commercial nonionic compounds of this general type which are also suitable include: Neodol 45-11, (also made by Shell Chemical Company); Alfonic 1618-65, which is a 16 to 18 carbon alkanol ethoxylated with an average of 10 to 11 mols of ethylene oxide per mol, manufactured by Continental Oil Company; and Plurafac B-26, manufactured by BASF-Wyandotte (ALFONIC and PLURAFAC are trade marks).

Instead of the preferred polyethoxylated higher fatty alcohols and similar alkanols there may also be used, at least in part, e.g., up to 25% or 50%, various other nonionic detergents such as are described at length in McCutcheon's *Detergents and Emulsifiers*, 1973 Annual and in the text book *Surface Active Agents*, Vol. II, by Schwartz, Perry and Berch (Interscience Publishers, 1958). Such nonionic detergents are usually pasty or waxy solvents at room temperature (20°C) and are either sufficiently water-soluble to dissolve promptly in water, especially in the presence of the hydrotrope, or quickly melt and disperse therein at the temperature of the wash water, as when that temperature is above 40° or 50°C. They will normally not be fluid at room temperature because in such state they might tend to make a tacky agglomerate of the final particulate detergent, which could be poorly flowing and could lump or set on storage. Typical useful nonionic detergents which may be employed, providing that they are satisfactorily detersive in the present compositions at the concentrations utilized, e.g., 0.1% to 0.2% of detergent composition in wash water, are the poly-lower alkenoxy derivatives that are usually prepared by the condensation of lower (2 to 4 carbon atoms) alkylene oxide, e.g., ethylene oxide, propylene oxide (with enough ethylene oxide to make a water-soluble product), with a compound having a hydrophobic e.g., hydrocarbon, chain containing one or more active hydrogen atoms, such as higher alkyl phenols, higher fatty acids, higher fatty mercaptans, higher fatty amines, higher fatty polyols and the higher fatty alcohols previously mentioned. Generally, such compounds will be alkoxylated with an average of about 3 to 30, preferably 3 to 15 and more preferably 7 to 11 alkylene oxide units. The most preferred nonionic detergents are those represented by the formula $RO(C_2H_4O)_nH$, wherein R is the residue of a linear saturated primary alcohol (an alkyl) of 12 to 15 carbon atoms and *n* is an integer from 7 to 11. Among additional nonionic detergents that may be employed are the Igepals (GAF Co. Inc.); Pluronics (BASF-Wyandotte) ; Poly-Tergents (Olin Corp.); and Amidoxes (Stepan Chemical Co.) (IGEPAL, PLURONIC, POLY-TERGENT and AMIDOX are trade marks).

In addition to the adjuvants previously mentioned, which are preferably post-added to the spray dried base particles, small proportions of anionic and amphoteric detergents may also be present in the base beads or may be post-added. These are not essential for the production of the desired detergent particles and if employed are normally present in small proportions, e.g., 0.5% to 2%. Examples of such materials include the alkali metal, preferably sodium, higher alkyl benzene sulphonates having 12 to 15 carbon atoms in their alkyl groups, which are preferably linear; higher fatty alcohol sulphates; higher alkyl sulphonates; higher olefin sulphonates; and polyethoxylated higher fatty alcohol sulphates. In such cases the higher alkyl or alkene groups are usually of 10 to 20 or 12 to 18 carbon atoms and polyethoxylation is to the extent of 3 to 30 or 3 to 15 alkylene oxides per mol. Instead of the synthetic anionic organic detergents mentioned the ordinary fatty acid soaps, usually sodium soaps of mixed higher fatty acids of 8 to 18 carbon atoms, such as those obtained from tallow and coconut oil, may desirably be substituted in whole or in part and mixtures of the anionic detergents may be used, with the total amount being within the percentage range previously given. Instead of the anionic detergents, amphoteric surface active agents may be employed. These are usually higher fatty carboxylates, phosphates, sulphates or sulphonates which contain a cation substituent such as an amino group which may be quaternized, for example, with lower alkyl groups, or may have the chain thereof extended at the amino group by condensation with a lower alkylene oxide, e.g., ethylene oxide. Representative commercial water-soluble amphoteric organic detergents include Deriphat 151 and Miranol C2M (DERIPHAT nad MIRANOL are trade marks). Sometimes it may be desirable to employ small proportions of cationic organic surface active agents, especially as anti-static or softening materials. Typical of such compounds are Ethoduomeens T/12 and T/13, which are ethylene oxide condensates of N-tallow trimethylene diamines and Ethylquad 18/12, 18/25 and 0/12, which are polyethoxylated quaternary ammonium chlorides (Armour Industries Chemical Co. - ETHODUDMEEN and ETHYLQUAD are trade marks). Various other synthetic detergents and surface active agents which may be employed are disclosed in the previously mentioned McCutcheon Annual and the Schwartz, Perry and Berch textbook.

To manufacture the low density particulate built synthetic organic detergent composition and the corresponding low density base composition particles, which are usually substantially inorganic with respect to the normally solid components thereof, an aqueous solution-dispersion, commonly referred to as a crutcher mix, is prepared, containing the various heat-resistant components of the final product, except the nonionic detergent and any materials best post-added. To save energy and to increase throughput of the drying equipment the crutcher mix will usually be of as high a solids content as feasible, e.g., 50% to 80%, with the balance, e.g. 20% to 50%, being water. More water may be used but then energy demands are increased, tower throughputs are diminished, products resulting may be tackier and poorer flowing and often the desired low density base and final detergent composition particles will not be obtained. Usually, when the moisture content of the crutcher mix is from 20% to 50% the water-soluble inorganic builder salt(s) content will be from 10% to 50%, the inorganic filler salt(s) content will be from 5% to 50% and the water-soluble, organic hydrotropic salt(s) content will be from 0.2% to 5%. When no inorganic filler salt is present the inorganic builder salt content may be such as to be the balance of the composition, in addition to the water and hydrotrope (and any other heat stable adjuvants, etc., present). Sodium tripolyphosphate, normally charged as pentasodium tripolyphosphate, is a preferred builder salt and usually constitutes at least half of the builder salt in the crutcher. Correspondingly, the preferred filler salt is sodium sulphate and generally this is at least half of the filler salt content in the crutcher mix. Of course, the content of water in the crutcher mix will be sufficient satisfactorily to dissolve-disperse the other components present.

Although other drying methods may be employed, such as drum drying, tray drying, fluidized bed drying, film drying, etc., the most preferred method is spray drying, wherein the crutcher mix is sprayed at an elevated pressure, usually from 3 to 50 kg/cm^2, preferably 20 to 40 kg/cm^2, through a spray nozzle into a drying tower, through which drying air passes to dry the resulting droplets of crutcher mix to globular, low density, free flowing particles. Instead of spray nozzles, equivalent atomizers of other designs may also be used. The preferred spray tower design is countercurrent, the height of the tower usually being from 5 to 25 metres and the entering hot air, usually the gaseous products of combustion of oil or gas, being at a temperature in the range from 200° to 400°C and the outlet air usually at a temperature in the range from 50° to 90°C. Concurrent tower designs may also be employed wherein similar inlet and outlet air temperatures obtain. It has been mentioned in German Offenlegungsschrift 2,514,677 that low density beads are more readily produced utilizing concurrent spray drying than result from countercurrent drying but with the method of the present invention low density products can be obtained with either type of tower. Countercurrent drying is preferred and has the benefits of greater efficiency of the drying operation because the thermal gradient for removal of the moisture in the partially dried product, near the exit of the tower, is greater.

The nozzle size for producing droplets of crutcher mix of desired size is chosen to produce base particles in the 6 to 160 mesh, U.S. Standard Sieve Series, range. Preferably, the product is substantially of particles in such range when it is removed from the spray tower but any off-size particles, such as may be from 2% to 10% by weight, may be removed by screening, may be size-reduced to the desired size range or may be recycled in the same or a subsequent crutcher mix. In some cases the 6 to 160 mesh product may be further screened to a narrower size range, such as 8 to 100 mesh. Also, spray characteristics may be altered so as to obtain substantially such a product from spray drying, without the need for further screening or size-reduction.

After drying is complete and the particles in the desired size range are obtained, the nonionic detergent is applied to the surfaces thereof, preferably by spraying molten detergent, which may be in concentrated aqueous solution but preferably is free of water, onto the surfaces of the tumbling base particles in an inclined drum, through which the particles progress from an elevated feed end to the discharge end. Instead of an inclined drum one may also use fluidized beds of various conventional designs and other commercial mixers, such as those of the Schugi type. The proportion of nonionic detergent, preferably polyethoxylated higher fatty alcohol, will desirably be from 4% to 15% and the beads onto which it is sprayed will contain from 3% to 16% moisture, preferably 5.6% to 13.3% and more preferably, 5.6% to 11.1% of water, so that the final product will comprise, respectively, 2.5% to 15%, 5% to 12%, or 5% to 10% of water. Of course, the moisture content of the base beads may be higher when additional moisture-free constituents are to be post-added.

The proportions of adjuvant materials will generally be held to less than 15%, preferably less than 10% and more preferably less than 5% total of the total produce and the proportions of individual adjuvants will be less than 5% each, preferably less than 2% each and more preferably less than 1%, e.g. 0.2 to 1%, each, in most cases.

If a bleaching agent, such as sodium perborate, usually as the tetrahydrate and activated, is to be incorporated with the detergent, greater percentages thereof, e.g., 5% to 40%, preferably 10% to 30%, may be present. Thus, sodium perborate is not considered as one of the ordinary adjuvants previously discussed. If used, it should be post-added.

For superior products it has been found desirable for the proportion of builder salt or filler salt to be within the range from 3:1 to 1:2, preferably 2:1 to 1:1.5. The bulk density of the base beads is in the range from 0.2 to 0.45 g/cc and that of the final product beads is in the range from 0.3 to 0.5 g/cc. Preferably the bulk densities will be from 0.2 to 0.35 and 0.3 to 0.45 g/cc, respectively.

Preferred detergent compositions of this invention comprise from 20% to 40% of sodium tripolyphosphate, 3% to 15% of sodium carbonate, 5% to 15% of sodium silicate of $Na_2O:SiO_2$ ratio in the range from 1:1.6 to 1:3, 0 to 5% of borax, 1% to 3% of sodium toluene sulphonate or sodium xylene sulphonate, 20% to 50% of sodium sulphate, 4% to 15% of higher fatty alcohol polyethylene oxide condensation product nonionic detergent and 5% to 12% of water. In such products the higher fatty alcohol ethylene oxide condensation product is one which melts or softens sufficiently to be sprayable in droplet form at a temperature below 45°C, and in the process of the invention it is melted and sprayed onto the surfaces of the spray dried particles of base material at a temperature below 55°C, while such particles are in motion and are at a temperature below 45°C and greater than 10°C. A highly preferably process is one wherein the moisture content of the crutcher mix is from 30% to 45%, the crutcher mix of such a composition as to result in a spray dried final detergent composition product which, when it includes from 7% to 13% of polyethoxylated higher fatty alcohol nonionic detergent post-added to the spray dried base beads, includes 28% to 38% of sodium tripolyphosphate, 3% to 8% of sodium carbonate, 5% to 10% of sodium silicate toluene sulphonate (or sodium xylene sulphonate), 0.5% to 2% of borax, 30% to 42% of sodium sulphate and 5% to 10% of moisture. In such a product the nonionic detergent is preferably a condensation product of a higher fatty alcohol of 12 to 15 carbon atoms and about 7 mols of ethylene oxide per mol of fatty alcohol, which product is sold under the trademark Neodol 25-7. In such process, the crutcher mix, at a temperature of 80° to 105°C, is sprayed into the spray drying tower, preferably a counter-current tower, with the tower drying air inlet temperature being in the range from 200° to 400°C, and the spraying is such as to result in droplets which dry to particles of a mixture of sizes substantially in the 6 to 160 mesh range. To produce such particles a nozzle orifice of a 0.2 to 0.8 mm diameter may be employed. In the post-spraying operation the nonionic detergent is sprayed onto the surfaces of the tumbling particles of base beads in a rotating inclined drum which may be at an angle of from 5° to 15° and which rotates at a speed of from 5 to 50 r.p.m. The nonionic detergent is at a temperature of from 35° to 50°C when sprayed on the tumbling particles, which are at a temperature of from 20° to 45°C.

The process for manufacture of the base or carrier beads has been described previously in conjunction with the overall process for the manufacture of detergent composition particles. However, allowing for about 10% of nonionic detergent being post-added to the base beads, the preferred and the most preferred contents of various components of the beads are somewhat different, being from 22% to 44% of sodium tripolyphosphate, 3.3% to 16.7% of sodium carbonate, 5.6% to 16.7% of sodium silicate, 1.1% to 3.3% of sodium toluene sulphonate or sodium xylene sulphonate, 0 to 5.6% of borax, 22% to 56% of sodium sulphate and 5.6% to 13.3% of water, the more preferred ranges being 31.1% to 42.2%; 3.3% to 8.9%; 5.6% to 11.1%; 1.3% to 2.2%; 0.5% to 2.2%; 33% to 47%; and 5.6% to 11.1%, respectively.

The various advantages of the described processes and the compositions resulting have been referred to previously but will be recounted briefly here. Principally, a built heavy duty nonionic detergent is manufactured which is in particulate form, of desired low density, non-tacky, non-caking and free flowing. It is made by an economical process which allows for ready variation in active detersive ingredient content of the composition. The process is environmentally acceptable, producing no undesirable smoke or fumes from the drying means, such as a spray tower. Also, tower throughput is increased and energy consumption is decreased. Despite the comparatively high contents of nonionic detergent in the final particulate composition such detergent is readily sorbed by the hydrotrope-containing beads and comparatively short mixing times, e.g., 1 to 5 minutes, are sufficient. The presence of the hydrotrope in the product, while not interfering with the properties of the nonionic detergent, does aid in solubilizing some comparatively insoluble soiling substances often present on laundry and also aids in promoting solubility of any poorly soluble adjuvants which may be present in the detergent composition, thus preventing unwanted depositing thereof onto the laundry. For example, colorante in detergent compositing may be prevented from being deposited on fabrics of the laundered items. However, the main advantage of the invention is in the production of desired low density particulate products and in this respect the present process, utilizing a hydrotropic salt of the type described, can produce a lower density product than is obtained with soap, mixtures of soap and nonionic detergent, and anionic detergents, employed in similar quantities.

The reason for the desirable effects noted with the present processes is not clear. It has been theorized that the hydrotropic salt aids in the production of a more homogeneous crutcher mix and thereby avoids the production of weak points or rupture-prone locations on the droplet or bead as drying is effected. Therefore, the bead can swell to a larger size and maintain such size as it is dried, leading to the production of a lower density product. However, even if such theory should become verified it would still be unexpected that the small proportion of hydrotropic salt utilized would be sufficiently effective significantly to modify the characteristics of a crutcher mix or base droplet containing such a high percentage of inorganic salts.

The detergent compositions of this invention, when employed in the same manner as conventional heavy duty particulate detergent compositions, at normal use concentrations, e.g., 0.1% to 0.2%, in cold, warm or hot wash waters, result in very satisfactory cleaning of the articles of laundry being washed. Additionally, the particulate detergent may be made into a paste with water for treatment of heavily soiled areas of the laundry and the presence of the hydrotrope assists in loosening such soil so that it may be more readily removed during washing.

The following Examples illustrate the invention. Unless otherwise mentioned, all parts and percentages in the specification are by weight.

EXAMPLE 1

A crutcher mix is made of 23.9% of sodium tripolyphosphate, 3.6% of sodium carbonate, 5.1% of sodium silicate, 1.1% of sodium toluene sulphonate, 0.7% of borax, 25.6% of sodium sulphate and 40% of water. All the components except the sodium silicate and the water are added as anhydrous powders. Sodium silicate is added as 10.2% of a 50% aqueous solution and its Na_2O:SiO_2 ratio is 1:2.35. The aqueous composition is mixed in a conventional heated detergent crutcher for a period of about 15 minutes (polyphosphate is added last) and is pumped by a high pressure pump (Triplex) at a pressure of 25 kg/cm^2 and at a temperature of 95°C into the top of a 20 m tall spray tower through a plurality of 0.5 mm dia. nozzles, which create a spray of droplets of sizes substantially in the 6 to 160 mesh, U.S. Standard Sieve Series, range, which produce beads of a similar size. The drying air, entering the bottom of the tower, is at a temperature of about 300°C and when it leaves the tower at the top it is at a temperature of about 90°C. The droplets of sprayed crutcher mix, falling through the tower, have an average residence time therein of about one minute, with residence time modifications, depending on particular drying conditions, being variable in the range from 30 seconds to 3 minutes. The spray dried beads, comprising over 95% of particles in the desired 6 to 160 mesh range, are withdrawn from the tower at a temperature of about 45°C, after some preliminary cooling at the base of the tower. The beads at this temperature are delivered to an inclined rotating drum wherein there is sprayed onto the surfaces thereof a melt of Neodol 25-7 (higher fatty alcohol mixture of about 12 to 15 carbon atoms polyethoxylated with about 7 mols of ethylene oxide per mol) at a temperature of about 40°C. The drum is inclined at an angle of about 7° and residence time of the particles therein is about 3 to 5 minutes. The spray nozzles are such that the droplets of spray are of sizes corresponding to about 100 to 200 mesh and the sprays are directed onto the surfaces of the tumbling particles. During the tumbling the product is cooled somewhat and after removal from the tumbling drum it is additionally cooled to a temperature in the 20° to 30°C range, after which it is ready for packaging.

The product made is an excellent heavy duty laundry detergent, especially good for cold and warm water use, wherein it is superior to many detergents based on anionic synthetic active ingredients. Its bulk density before packaging is about 0.34 g/cc, having been increased slightly during the add-on of nonionic detergent, from about 0.29 g/cc. The moisture content to which the crutcher mix content had been dried to form the base beads is 7.7%. The final detergent composition is of the following analysis: 33% sodium tripolyphosphate; 5% sodium carbonate; 7% sodium silicate; 1.5% sodium toluene sulphonate; 1% borax; 35.5% sodium sulphate; 10% nonionic detergent; and 7% water.

In a control experiment, when the same operational steps are repeated with the same composition except that the sodium toluene sulphonate is omitted from the crutcher mix, the density of the spray dried base beads resulting is over 0.5 g/cc and that of the finished detergent composition particles is 0.59 g/cc, which is objectionably high for a product designed to be commercially marketed in replacement of conventional spray dried detergent compositions.

In modifications of the process of the invention the drying of the crutcher mix is effected by drum and tray drying and the products resulting are size reduced to the desired 6 to 160 mesh and narrower ranges. By such method a desirable lowering of the density of the product into the 0.3 to 0.5 g/cc range is obtained whereas without the presence of the hydrotropic salt a higher density, outside such range, may result. The bulk density may be desirably lowered further by aerating the mix before drying, with the hydrotropic salt present therein. Also, further lowerings of the bulk density of the drum dried and tray dried products, as well as those made by spray drying, as described above, are obtained when the particle size ranges are from 8 to 140 and 8 to 100 mesh, with particles outside such ranges being removed and subjected to size reduction or recycling treatments.

In other modifications of the described experiment, utilizing spray drying, the proportions of the various components of the crutcher mix are individually modified, ±10%, ±20% and ±30%, while still remaining in the ranges specified, with the proportions of other components remaining constant. In such cases the processing conditions are also changed, with the crutcher mix temperature being modified to 85°, 90° and 100°C, the spray nozzle cross-sectional area being increased and decreased 10% and the drying air inlet temperature being changed to 250° and 350°C in various experiments. Also, in addition to utilizing the inclined drum described, the angle thereof is modified to 5° and 12° and in some cases the nonionic detergent is applied in a Schugi apparatus or is directed into a fluidized bed of the base particles. The temperature of the base beads is changed ±5°C, as is that of the nonionic detergent being sprayed onto them. In some instances 0.6% of perfume is added with the nonionic (dissolved therein). In all such cases useful products of the present invention are obtained, with the properties thereof being as described and within the mentioned desirable ranges.

EXAMPLE 2

The procedure of Example 1 is repeated, with sodium xylene sulphonate being substituted for sodium toluene sulphonate, and essentially the same types of low density base and final products are obtained. When sodium benzene sulphonate is utilized instead, acceptable products result but the effects thereof are not considered to be as good as those with the methyl-substituted benzene sulphonates. When the potassium salts of the mentioned hydrotropes are used, including potassium toluene sulphonate, essentially the same types of detergent compositions are produced.

When the previous experiments are repeated, but with substitutions of Neodol 45-11 and Alfonic 1618-65 for the Neodol 25-7, similar results are obtained. When pentasodium tripolyphosphate is replaced by tetrasodium pyrophosphate and when, in manufacturing non-phosphate detergents, the sodium tripolyphosphate is completely replaced by a mixture of two parts of sodium carbonate and one part of sodium silicate, products within the specifications of this invention are obtainable. This is also the case when sodium sulphate is replaced by sodium chloride or is omitted entirely, with the difference being made up by increases in sodium tripolyphosphate and sodium carbonate, and when sodium silicates of Na_2O:SiO_2 ratios of 1:2.O and 1:2.4 are used.

Our co-pending British patent application No. 50119/77 (Serial No. 1591515) describes and claims a free flowing, particulate, detergent-fabric softener composition of bulk density of at least 0.6 g/cc and particle sizes in the range from 4 to 40 mesh which comprises nucleus particles of an alkali metal builder salt selected from sodium carbonate mixed with sodium bicarbonate, sodium carbonate, sodium bicarbonate, pentasodium tripolyphosphate, tetrasodium pyrophosphate, sodium silicate, borax, corresponding potassium salts, and mixtures thereof, containing a normally liquid or pasty nonionic detergent in the interiors of such particles and on the surfaces thereof and coated with ion exchanging zeolite particles adhered to the nonionic detergent on the builder particle surfaces, and a waxy quaternary ammonium compound softening agent external to or within the particles.

It also described and claims a method of making such a detergent-fabric softener composition which comprises mixing together the alkali metal builder, the nonionic detergent and the softening agent, the nonionic detergent and the softening agent being in liquid form during the mixing, so that they are absorbed in and coat the builder, and admixing with the coated particles zeolite particles of ultimate particle sizes in the range from 0.01 to 20 microns, which zeolite particles adhere to the detergent and softening agent on the surfaces of the coated particles, to make them free flowing.

Our co-pending British patent application No. 50121/77 (Serial No. 1591517) describes and claims a free-flowing, particulate, heavy duty laundry detergent composition of a bulk density of at least 0.6 g/cc and a particle size in the range from 4 to 140 mesh which comprises granules containing: (a) sodium tripolyphosphate particles, these particles having a bulk density in the range from 0.4 to 0.8 g/cc, a size in the range from 8 to 140 mesh and a sodium tripolyphosphate content of at least 60% by weight; (b) water-insoluble aluminosilicate zeolite having a calcium ion exchange capacity in the range from 200 to 400 milligram equivalents of calcium carbonate hardness per gram of aluminosilicate, the zeolite being selected from crystalline, amorphous and mixed crystalline-amorphous zeolites, having a water content from 1.5% to 36% and having an ultimate particle diameter in the range from 0.01 to 20 microns; and (c) a water-soluble nonionic detergent which is a condensate of a compound having a hydrophobic carbon chain of at least 8 carbon atoms with a water-solubilizing C_2 - C_4 alkylene oxide chain and which is in liquid or pasty form at room temperature; the granules having the nonionic detergent in the interior and on the surfaces of the tripolyphosphate particles, and the percentages by weight of sodium tripolyphosphate particles, zeolite particles and nonionic detergent being in the ranges from 30% to 50%, 30% to 50% and 5% to 30%, respectively.

It also describes and claims a method of making such a free-flowing, particulate, heavy duty laundry detergent composition which comprises mixing together the sodium tripolyphosphate particles and the zeolite particles at a temperature of at least 10°C for a period in the range from 30 seconds to 10 minutes, and then admixing with such mixture a nonionic detergent in liquid form so that the detergent penetrates the sodium tripolyphosphate particles and adheres the zeolite particles to the surfaces thereof.

Our co-pending British patent application No. 50122/77 (Serial No. 1591518) describes and claims a free flowing, particulate, heavy duty laundry detergent composition of bulk density of at least 0.6 g/cc and particle sizes in the range from 4 to 40 mesh which comprises nucleus particles in the range from 20 to 100 mesh of alkali metal carbonate and alkali metal bicarbonate wherein the weight ratio of alkali metal carbonate to alkali metal bicarbonate is in the range from 1:10 to 10:1 containing and coated with a normally liquid or pasty water-soluble ethoxylated nonionic detergent having a hydrophobic group containing from 8 to 20 carbon atoms in its molecular structure, which nonionic detergent coating is further coated with particles of a calcium ion exchanging water-insoluble zeolite aluminosilicate of a univalent cation having ultimate particle diameters in the range from 0.005 to 20 microns, the weight percentages of mixed alkali metal carbonate and alkali metal bicarbonate, zeolite and nonionic detergent being in the ranges from 20% to 40%, from 40% to 60% and from 10% to 30%, respectively.

It also describes and claims a method of making such a free-flowing, particulate, heavy duty laundry detergent composition which comprises mixing together the nucleus particles, and the nonionic detergent in liquid form, so that the detergent is absorbed by and coats the particles, and admixing with such coated particles the zeolite particles which adhere to the detergent on the surfaces of the detergent-coated particles to form the specified coated particles which are in the size range from 4 to 40 mesh and are free-flowing.

WHAT WE CLAIM IS:-

1. A process for manufacturing a low density substantially inorganic particulate base composition useful for conversion to a built synthetic organic detergent composition by addition of nonionic detergent thereto, which comprises mixing together a plurality of components of a crutcher mix, including inorganic builder(s), water-soluble organic hydrotropic salt(s) and water in such proportions that when subsequently dried the water-soluble organic hydrotropic salt(s) present significantly-reduce(s) the density of the product, and drying the mix.

2. A process accordingto Claim 1 wherein the crutcher mix comprises from 20% to 50% of water, from 10% to 50% of water-soluble inorganic filler salt(s) and from 0.2% to 5% of water-soluble organic hydrotropic salt(s) of a substituted or unsubstituted benzene sulphonic acid, and the crutcher mix is spray dried.

3. A process according to Claim 2 wherein at least half of the builder salt is sodium tripolyphosphate, at least half of the filler salt is sodium sulphate, the hydrotrope is a water-soluble salt of a lower alkyl substituted benzene sulphonic acid and the spray drying is effected in a countercurrent tower.

4. A process according to Claim 3 wherein the builder salt comprises sodium tripolyphosphate, sodium silicate and sodium carbonate, substantially all of the filler salt is sodium sulphate, the hydrotrope is a water soluble salt of a mono-or di-methyl substitute benzene sulphonic acid, the proportion of builder salt to filler salt is in the range from 3:1 to 1:2, and the crutcher mix is spray dried to a moisture content in the range from 3% to 16% and a bulk denisty in the range from 0.2 to 0.45 g/cc.

5. A process according to Claim 4 wherein the proportions of the components of the crutcher mix are such that the spray dried product comprises from 22% to 44% of sodium tripolyphosphate, from 3.3% to 16.7% of sodium carbonate, from 5.6% to 16.7% of sodium silicate, from 1.1% to 3.3% of sodium toluene sulphonate and/or sodium xylene sulphonate, from 0 to 5.6% of borax, 22% to 56% of sodium sulphate and 5.6% to 13.3% of water.

6. A process according to Claim 11 wherein the moisture content of the crutcher mix is from 30% to 45%, the crutcher mix is of such composition as to result in a spray dried particulate base product comprising from 31.1% to 42.2% of sodium tripolyphosphate, from 3.3% to 8.9% of sodium carbonate, from 5.6% to 11.1% of sodium silicate of $Na_2O:SiO_2$ ratio in the range from 1:2 to 1:2.4, from 1.3% to 2.2% of sodium toluene sulphonate, from 0.5% to 2.2% of borax, from 33% to 47% of sodium sulphate and from 5.6% to 11.1% of water, the crutcher mix is at a temperature from 80 to 105°C when it is sprayed into the spray drying tower, the tower drying air inlet temperature is in the range from 200° to 400°C and the crutcher mix is sprayed into the tower and forms droplets of such size as to result in dried particles of a mixture of sizes substantially in the 6 to 160 mesh range.

7. A process for manufacturing a low density substantially inorganic particulate base composition useful for conversion of a built synthetic organic detergent composition by addition of nonionic detergent thereto, as claimed in Claim 1 and substantially as described in either of the Examples.

8. A low density substantially inorganic particulate base composition useful for conversion to a built synthetic organic detergent composition by addition of nonionic detergent thereto, which has been manufactured by a process according to any of the preceding Claims.

9. A low density substantially inorganic particulate base composition useful for conversion to a built synthetic organic detergent composition by addition of nonionic detergent thereto, which comprises from 22% to 44% of sodium tripolyphosphate, from 3.3% to 16.7% of sodium carbonate, from 5.6% to 16.7% of sodium silicate of $Na_2O:SiO_2$ ratio in the range from 1:1.6 to 1:3, from 1.1% to 3.3% of sodium toluene sulphonate and/or sodium xylene sulphonate, 0 to 5.6% of borax, from 22% to 56% of sodium sulphate and from 5.6% to 13.3% of water.

10. A composition according to Claim 9, of particle sizes in the 6 to 160 mesh range and comprising from 31.1% to 42.2% of sodium tripolyphosphate, from 3.3% to 8.9% of sodium carbonate, from 5.6% to 11.1% of sodium silicate of $Na_2O:SiO_2$ ratio in the range from 1:2 to 1:2.4, from 1.3% to 2.2% of sodium toluene sulphonate and/or sodium xylene sulphonate from 0.5% to 2.2% of borax, from 33% to 47% of sodium sulphate and from 5.6% to 11.1% of water.

11. A process for manufacturing a low density particulate built synthetic organic detergent composition which comprises applying onto the surfaces of particles of a particulate base composition according to any of claims 8 to 10 a detersive proportion of nonionic detergent.

12. A process according to Claim 11 wherein the nonionic detergent is a polyethoxylated higher fatty alcohol in a proportion to constitute from 5 to 25% of the product.

13. A process according to Claim 12 wherein the polyethoxylated fatty alcohol is a condensation product of a fatty alcohol of 10 to 18 carbon atoms and 3 to 15 mols of ethylene

oxide per mol of fatty alcohol.

14. A process according to Claim 13 wherein the fatty alcohol ethylene oxide condensation product is one which melts or softens sufficiently to be sprayable in droplet form at a temperature below 45°C and is melted and sprayed onto the surfaces of the spray dried particles at a temperature below 55°C when the particles are in motion and are at a temperature below 45°C and greater than 10°C.

15. A process for manufacturing a low density particulate built synthetic organic detergent composition which comprises mixing together a plurality of components of a crutcher mix, including inorganic builder(s), water-soluble organic hydrotropic salt(s) and water in such proportions that when subsequently dried the water-soluble organic hydrotropic salt(s) present significantly reduce(s) the density of the product, drying the mix and applying onto the surfaces of particles of the dried mix a detersive proportion of nonionic detergent and wherein the moisture content of the crutcher mix is in the range from 30% to 45%, the crutcher mix is of such composition as to result in a spray dried product, when it contains from 7% to 13% of polyethoxylated higher fatty alcohol nonionic detergent which is post-sprayed onto the spray dried composition, from 28% to 38% of sodium tripolyphosphate, from 3% to 8% of sodium carbonate, from 5% to 10% of sodium silicate of Na_2O:$WioO_2$ ratio in the range from 1:2 to 1:2.4, from 1.2% to 2% of sodium toluene sulphonate, from 0.5% to 2% of borax, from 30% to 42% of sodium sulphate and from 5% to 10% of moisture, the nonionic detergent is a condensation product of a fatty alcohol of 12 to 15 carbon atoms and about 7 mols of ethylene oxide per mol of fatty alcohol, the crutcher mix is at a temperature in the range from 80° to 105°C when it is sprayed into the spray drying tower, the tower drying air inlet temperature is in the range from 200° to 400°C, the crutcher mix is sprayed into the tower and forms droplets of such size as to result in dried particles of a mixture of sizes substantially in the 6 to 160 mesh range, and the post spraying of nonionic detergent is onto the surfaces of tumbling particles in a rotating inclined drum with the nonionic detergent at a temperature in the range from 35° to 50°C and the tumbling particles at a temperature in the range from 20° to 45°C.

16. A process according to any of Claims 11 to 15 which is so conducted as to produce a resulting particulate product having a bulk density in the range from 0.3 to 0.5 g/cc.

17. A process for manufacturing a low density particulate built synthetic organic detergent composition as claimed in Claim 11 and substantially as described in either of the Examples.

18. A low density particulate built synthetic organic detergent composition which has been manufactured by a process according to any of Claims 11 to 17.

19. A particulate built nonionic detergent composition having a bulk density in the range from 0.3 to 0.5 g/cc which comprises from 20% to 40% of sodium tripolyphosphate, from 3% to 15% of sodium carbonate, from 5% to 15% of sodium silicate of Na_20:SiO_2 ratio in the range from 1:6 to 1:3, from 1% to 3% of sodium toluene sulphonate and/or sodium xylene sulphonate, 0 to 5% of borax, from 20 to 50% of sodium sulphate, from 4% to 5% of polyethoxylated fatty alcohol nonionic detergent which is a condensation product of fatty alcohol(s) of 10 to 18 carbon atoms and 3 to 15 mols of ethylene oxide per mol of fatty alcohol, and from 5% to 12% of water.

20. A composition according to Claim 19 wherein the nonionic detergent is one which melts or softens sufficiently to be sprayable in droplet form at a temperature below 45°C and coats base particles comprising the other named composition constituents and the particles are substantially of sizes in the 6 to 160 mesh range.

21. A composition according to Claim 20 comprising from 28% to 38% of sodium tripolyphosphate, from 3% to 8% of sodium carbonate, from 5% to 10% of sodium silicate of Na_2O:SiO_2 ratio in the range from 1:2 to 1:2.4, from 1.2% to 2% of sodium toluene sulphonate, 0 to 2% of borax, from 30% to 42% of sodium sulphate, from 7% to 13% of polyethoxylated fatty alcohol nonionic detergent and from 5% to 10% of moisture.

22. A composition according to Claim 21 wherein the nonionic detergent is a condensation product of a fatty alcohol of from 12 to 15 carbon atoms and about 7 mols of ethylene oxide per mol fatty alcohol.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.