

[54] Title: BASE BEADS FOR MANUFACTURE OF DETERGENT COMPOSITION

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U.S. Pat. No. 4,264,464 April /1981 Gangvish
4,311,607 Jan. 19, 1982 James A. Kaeber

[57]

ABSTRACT

Free-flowing base beads, into which nonionic detergent in liquid form may be absorbed to make a free-flowing particulate built synthetic nonionic organic detergent product of improved washing properties, include 15 to 50% of sodium carbonate, 10 to 22% of sodium bicarbonate, 20 to 50% of water softening aluminum silicate (zeolite), 4 to 12% of sodium silicate, 1 to 15% of bentonite and 1 to 15% of moisture, together with suitable adjuvants and processing aids in small proportions (normally totalling less than 10% and preferably less than 5%). Preferably the content of sodium silicate is in the range of 5 to 10% and that of bentonite is in substantially the same range. At such concentrations in the base beads, the use of detergent compositions made from them by absorption of nonionic detergent, so that the product contains from about 8 to 25% nonionic detergent, under adverse washing conditions, i.e., cold water, high water hardness (as calcium carbonate) and gentle agitation, will result in less residue being deposited on washed materials than when control see attached sheet

16 Claims. Specification: 47 page (s): Drawings: None sheet (s)
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Attorney / Agent: BITO, ET AL.

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Cont. ABSTRACT

detergent products, from which bentonite is omitted, are employed. The beads, the detergent, compositions made from them and the methods for their manufacture are further improved by incorporation of a small proportion, e.g., 0.2 to 2%, of a low molecular weight polyacrylate in crutcher mixes from which the beads may be made by spray drying. ~~xxxx~~

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SPECIFICATION

Be it known that I, John Jerome Grecsek, have invented new and useful "BASE BEADS FOR MANUFACTURE OF DETERGENT COMPOSITIONS" of which the following is the specification.

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ABSTRACT OF THE DISCLOSURE:

5 Free-flowing base beads, into which nonionic
detergent in liquid form may be absorbed to make a free-
flowing particulate built synthetic nonionic organic detergent
product of improved washing properties, include 15 to 30% of
sodium carbonate, 10 to 22% of sodium bicarbonate, 20 to 40%
10 of water softening aluminum silicate (zeolite), 4 to 12% of
sodium silicate, 1 to 15% of bentonite and 1 to 15% of
moisture, together with suitable adjuvants and processing
aids in small proportions (normally totalling less than 10%
and preferably less than 5%). Preferably the content of
15 sodium silicate is in the range of 5 to 8% and that of benton-
ite is in substantially the same range. At such concentrations
in the base beads, the use of detergent compositions made
from them by absorption of nonionic detergent, so that the
product contains from about 8 to 25% nonionic detergent,
20 under adverse washing conditions, i.e., cold water, high
water hardness (as calcium carbonate) and gentle agitation,
will result in less residue being deposited on washed
materials than when control detergent products, from which
bentonite is omitted, are employed. The beads, the detergent

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compositions made from them and the methods for their manufacture are/further improved by incorporation of a small proportion, e.g., 0.2 to 2%, of a low molecular weight polyacrylate in crutcher mixes from which the beads may be
5 made by spray drying.

This invention relates to base beads which are useful for the manufacture of built nonionic detergent compositions. More particularly, it relates to such beads which are essentially inorganic in nature and include sodium
10 carbonate, sodium bicarbonate, zeolite, sodium silicate and bentonite, and which may absorb nonionic detergent, in liquid form, to make freely flowing, particulate, built nonionic detergent compositions. The invention also relates to the detergent compositions made, which are of improved washing
15 properties, depositing less residue on washed materials despite the presences of zeolite and silicate.

Synthetic organic detergent compositions containing water softening aluminum silicates, such as zeolites, have been invented and marketed in recent years. In such
20 compositions, which also include a synthetic organic detergent or surface active agent component, the zeolite acts as a calcium sequestrant and as a builder for the organic detergent, improving its cleaning effects, especially in

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hard water. In such compositions sodium silicate has also been employed as a builder and as a corrosion preventing additive, to protect aluminum parts of washing equipment with which aqueous solutions of the detergent composition
5 come in contact during washing operations. The silicates also may be useful in counteracting any adverse effects magnesium ions in the wash water could have on the washing activity of the detergent composition. Additionally, it is considered that the silicate helps to produce more stable
10 detergent beads, especially when such are made by spray drying of a crutcher mix of detergent composition components. However, it is well recognized that zeolites often tend to deposit as a noticeable residue on laundry washed in aqueous cleaning media containing them, and various investigators
15 have reported that the presence of a silicate in such a medium with zeolite increases the amount of residue deposited.

Bentonite, a swelling clay, with comparatively minor hardness ion exchange capacity, has been suggested for use in various detergent product, such as soap bars and
20 laundry detergents, wherein it has often served primarily as a filler. However, in some instances it is alleged to perform other functions. For example, in U.S. patent 4,166,039 it is taught to aid in the production of homogeneous detergent slurries when such slurries contain
25 phosphate(s). Normally however, the incorporation of clays in detergent compositions is avoided because they are

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insoluble and might be expected to deposit on the materials being laundered. In fact, clay soil removal is one of the tests utilized to rate detergent effectiveness. Despite the fact that it might be expected that the addition of bentonite
5 would only exacerbate residue problems encountered when washing laundry with aqueous media containing detergent compositions incorporating zeolite and silicate, surprisingly it has been found that residue deposition is diminished. Also, calcium ion binding rates are increased.

10 In accordance with the present invention free flowing base beads, on which nonionic detergent may be absorbed to make particulate built synthetic nonionic organic detergent products of improved washing properties, which, after rinsing, leave lesser amounts of deposits on fabrics
15 washed with such products, comprise by weight from about 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 20 to 40% of water softening aluminum silicate, 4 to 12% of sodium silicate and 1 to 15% of bentonite. Such products will normally contain from 1 to 15% of moisture and may be
20 made into organic detergent compositions/ by application of liquid state nonionic detergent to them so that the detergent is absorbed and the product resulting is still free flowing. The proportion of detergent utilized will be such that the final product will contain about 8 to 25% thereof, by weight.
25 In additionally preferred embodiments of the invention the base beads will contain from about 0.1 to 2% of a relatively low molecular weight polyacrylate and the detergent compositions

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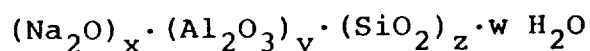
will contain a corresponding but reduced proportion (reduced due to the addition of nonionic detergent). The presence of the polyacrylate helps to make the base beads more absorptive of the liquid nonionic detergent. Also, it often
5 improves spray drying operations, resulting in less material adhering to the dryer walls and thereby increasing spray tower throughput rates and diminishing the number of clean-outs which may be required.

The various components of the base beads of this
10 invention, except for water, are normally in the solid state, although, when added to the crutcher, some may be in the forms of hydrates or may be dissolved or dispersed in an aqueous medium, such as water. The sodium bicarbonate is anhydrous and sodium carbonate is generally utilized as soda,
15 ash. Yet, the carbonate hydrates, such as the monohydrate, may be employed, if desired, and in some cases it may be possible to utilize other carbonates and bicarbonates, such as other alkali metal salts, e.g., the potassium salts, in replacement of at least some of the sodium salt, although the
20 sodium salts are highly preferred. The silicate is usually added to the crutcher as an aqueous solution, which is normally of 40 to 50% solids content, e.g., 47.5%, and preferably its addition is near the end of the mixing process. The silicate employed will usually be of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio
25 within the range of $\frac{1}{1}:\frac{1}{1.6}$ to $\frac{1}{1}:\frac{1}{2.6}$, preferably 1:1.6 to 1:2.4 and more preferably 1:2 to 1:2.4. Although sodium silicate is the preferred silicate, a portion of the sodium silicate may be replaced by potassium silicate or other suitable soluble alkali metal silicate salt.

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The zeolites employed include crystalline, amorphous and mixed crystalline-amorphous zeolites of both natural and synthetic origins which are of satisfactorily quick and sufficiently effective activities in counteracting calcium hardness ions in wash waters. Preferably, such materials are capable of reacting sufficiently rapidly with the calcium ions so that, alone or in conjunction with other water softening compounds in the detergent, they soften the wash water before adverse reactions of such ions with other components of the synthetic organic detergent composition occur. The zeolites employed may be characterized as having a high exchange capacity for calcium ion, which is normally from about 200 to 400 or more milligram equivalents of calcium carbonate hardness per gram of the aluminosilicate, preferably 250 to 350 mg. eq./g. Also they preferably have a hardness depletion rate residual hardness of 0.02 to 0.05 mg. CaCO₃/liter in one minute, preferably 0.02 to 0.03 mg./l., and less than 0.01 mg./l. in 10 minutes, all on an anhydrous zeolite basis.

Although other ion exchanging zeolites may also be utilized, normally the finely divided synthetic zeolite builder particles employed in the practice of this invention will be of the formula



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wherein x is 1, y is from 0.8 to 1.2, preferably about 1, z is from 1.5 to 3.5, preferably 2 to 3 or about 2 and w is from 0 to 9, preferably 2.5 to 6.

The zeolite should be a univalent cation-exchanging
5 zeolite, i.e., it should be an aluminosilicate of a univalent cation such as sodium/ potassium, lithium (when practicable) or other alkali metal, ammonium or hydrogen (sometimes). Preferably the univalent cation of the zeolite molecular sieve is an alkali metal cation, especially sodium or potas-
10 sium, and most preferably is sodium.

Crystalline types of zeolites utilizable as good ion exchangers in the invention, at least in part, include zeolites of the following crystal structure groups: A, X, Y, L, mordenite and erionite, of which types A, X and Y are
15 preferred. Mixtures of such molecular sieve zeolites can also be useful, especially when type A zeolite is present. These crystalline types of zeolites are well known in the art and are more particularly described in the text Zeolite Molecular Sieves by Donald W. Breck, published in
20 1974 by John Wiley & Sons. Typical commercially available zeolites of the aforementioned structural types are listed in Table 9.6 at pages 747-749 of the Breck text, which table is incorporated herein by reference. Also, suitable zeolites have been described in many patents in recent years for use
25 as detergent composition builders.

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The zeolite used in the invention is usually synthetic and it is often characterized by having a network of substantially uniformly sized pores in the range of about 3 to 10 Angstroms, often being about 4 Å (normal), such size being uniquely determined by the unit structure of the zeolite crystal. Preferably it is of type A or similar structure, particularly described at page 133 of the aforementioned text. Good results have been obtained when a Type 4A molecular sieve zeolite is employed, wherein the univalent cation of the zeolite is sodium and the pore size of the zeolite is about 4 Angstroms. Such zeolite molecular sieves are described in U.S. patent 2,882,243, which refers to them as Zeolite A.

Molecular sieve zeolites can be prepared in either a dehydrated or calcined form which contains from about 0 or about 1.5% to about 3% of moisture or in a hydrated or water loaded form which contains additional bound water in an amount from about 4% up to about 36% of the zeolite total weight, depending on the type of zeolite used. The water-containing hydrated form of the molecular sieve zeolite (preferably about 15 to 70% hydrated) is preferred in the practice of this invention when such crystalline product is used. The manufacture of such crystals is well known in the art. For example, in the preparation of Zeolite A, referred to above, the hydrated zeolite crystals that are formed in the crystallization medium (such as a hydrous amorphous sodium aluminosilicate gel) are used without the

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high temperature dehydration (calcining to 3% or less water content) that is normally practiced in preparing such crystals for use as catalysts, e.g., cracking catalysts.

The crystalline zeolite, in either completely hydrated or partially hydrated form, can be recovered by filtering off the crystals from the crystallization medium and drying them in air at ambient temperature so that their water contents are in the range of about 5 to 30% moisture, preferably about 10 to 25%, such as 17 to 22%. However, the moisture content of the molecular sieve zeolite being employed may be much lower, as was previously described, in which case the zeolite will usually be hydrated during crutching and other processing.

Preferably the zeolite should be in a finely divided state with the ultimate particle diameters being up to 20 microns, e.g., 0.005 or 0.01 to 20 microns, preferably being from 0.01 to 15 microns and especially preferably of 0.01 to 8 microns mean particle size, e.g., 3 to 7 or 12 microns, if crystalline, and 0.01 to 0.1 micron, e.g., 0.01 to 0.05 micron, if amorphous. Although the ultimate particle sizes are much lower, usually the zeolite particles will be of sizes within the range of 100 to 400 mesh, preferably 140 to 325 mesh. Zeolites of smaller sizes will often become objectionably dusty and those of larger sizes may not sufficiently and satisfactorily cover the carbonate-bicarbonate base particle nuclei on which they may be deposited

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during spray drying of a crutcher mix to form the base beads.

The bentonite employed is a colloidal clay (aluminum silicate) containing montmorillonite. Montmorillonite is a hydrated aluminum silicate in which about 1/6th of the aluminum atoms may be replaced with magnesium atoms and with which varying amounts of hydrogen, sodium, potassium, calcium, magnesium and other metals may be loosely combined. The type of bentonite clay which is useful in making the invented base beads is that which is known as sodium bentonite (or Wyoming or western bentonite), which is normally a light to cream-colored impalpable powder which, in water, forms a colloidal suspension having strongly thixotropic properties. In water the swelling capacity of the clay will usually be in the range of 3 to 15 ml./gram, preferably 7 to 15 ml./g. and its viscosity, at a 6% concentration in water, will usually be in the range of 3 to 30 centipoises, preferably 8 to 30 centipoises. Preferred swelling bentonites of this type are sold under the trademark THIXO-JEL, as industrial bentonites, by Benton Clay Company, an affiliate of Georgia Kaolin Co. Such materials are selectively mined and beneficiated bentonites, and those considered to be most useful are available as THIXO-JEL's No's. 1, 2, 3 and 4. Such materials are of pH's (6% concentration in water) in the range of 8 to 9.4, maximum free moisture contents of about 8% and specific

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gravities of about 2.6, and for the pulverized grade about 85% passes through a 200 mesh U.S. Sieve Series sieve. Such materials exhibit an exchangeable calcium oxide percentage in the range of about 1 to 1.8 and with respect to magnesium oxide such percentage is normally in the range of 0.04 to 0.41. Typical chemical analyses of such materials are from 64.8 to 73.0% of SiO_2 , 1.4 to 1.8% of Al_2O_3 , 1.6 to 2.7% of MgO , 1.3 to 3.1% of CaO , 2.3 to 3.4% of Fe_2O_3 , 0.8 to 2.8% of Na_2O and 0.4 to 7.0% of K_2O .

The only other material necessary for making the present beads is water, and during drying of the beads the moisture content thereof may be decreased so that the product is almost anhydrous. While it is preferred to employ deionized water, so that the hardness ion contents thereof may be very low and so that metallic ions that can promote decomposition of any organic materials which may be present in the final beads and detergent are minimized, normal city or tap water may be used instead. Normally the hardness content of such water will be less than 150 p.p.m., as CaCO_3 , more preferably the hardness content will be less than 100 p.p.m. and most preferably it will be less than 50 p.p.m.

The polyacrylate, present in preferred base beads of this invention, is a low molecular weight polyacrylate, such molecular weight usually being within the range of about 1,000 to 5,000, preferably 1,000 to 3,000, and most preferably 1,000 to 2,000 or about 2,000. The polyacrylate may be partially neutralized or completely neutralized, e.g.,

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about 1/2 or 1/3 Na salt. Although modified polyacrylates may be substituted for the described sodium polyacrylate, including some other alkali metal polyacrylates and hydroxylated polyacrylates, it is preferred that such
5 substitutions be limited to a minor proportion of the material and preferably the polyacrylate will be an unsubstituted sodium polyacrylate. Such materials are available from Alco Chemical Corporation under the name Alcosperse. The sodium/polyacrylates are available as clear amber
10 liquids or powders, with the solutions being of about 25 to 40% solids content, e.g., 30%, and with the pH of such solutions or of a 30% aqueous solution of the powder being in the range of about 7.5 to 9.5, e.g., about 9. Such materials are completely soluble in water and have been
15 employed as dispersants. They have been shown to possess the capability of binding calcium ion and have been used to prevent depositing out of insoluble calcium compounds from aqueous solutions.

Because fairly concentrated aqueous crutcher mixes
20 of silicate, carbonate, bicarbonate, zeolite and bentonite, with or without polyacrylate present, may "freeze" in the crutcher due to interactions of the components thereof, if held beyond a permissible time, processing aids are preferably present in the crutcher, and consequently, in the
25 finished base beads and detergent composition, to prevent

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premature solidification or gelation of the mix. Most preferably, such include citric acid and magnesium sulfate. Instead of citric acid, soluble citrates, such as sodium citrate, may be used and while it is preferable to employ anhydrous magnesium sulfate, various hydrates thereof, such as epsom salts, may also be used. Also, magnesium citrate can be substituted. In place of the preferred anti-gelling system other means and suitable systems for maintaining the crutcher mix fluid may be substituted, such as sodium sesquicarbonate, employed in replacement of some of the sodium carbonate and sodium bicarbonate.

Various adjuvants, such as perfumes, enzymes, colorants, bleaches and flow promoting agents may often be sprayed onto or otherwise mixed with the base beads after the manufacture thereof, with the nonionic detergent or separate from it, so that they are not adversely affected by the spray drying operation and also, so that their presence in the spray dried beads does not inhibit absorption of nonionic detergent. However, for stable and normally solid adjuvants, mixing in with the inorganic salts slurry in the crutcher is also feasible. Thus, it is contemplated that coloring agents and fluorescent brightener will normally be present in the crutcher mix from which the present base beads are sprayed. The preferred coloring agent is ultramarine blue but other stable pigments and dyes may be used

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with it or in replacement of it. Among the fluorescent brighteners the most preferred is Tinopal 5BM. However, various other cotton brighteners, such as those sometimes referred to as CC/DAS brighteners derived from the reaction product of cyanuric chloride and the disodium salt of diamino-
5 stilbene disulfonic acid, may also be employed, including variations thereof with respect to substituents on the triazine and aromatic rings. This class of brighteners is known in the detergent art and will most often be used when
10 bleaching components are not present in the final product. In such instances bleach stable brighteners may be employed. Among these may be mentioned the benzidine sulfone disulfonic acids, naphthotriazolyl stilbene sulfonic acids and benzimidazolyl derivatives. Polyamide brighteners, which also
15 may be present, include aminocoumarin or diphenyl pyrazoline derivatives and polyester brighteners, which can also be used, include naphthotriazolyl stilbenes. All such brighteners are normally used as their soluble salts but they may also be charged as the corresponding acids. The cotton
20 brighteners will usually comprise major proportions of the brightener systems.

Of the materials that may be post-added to the spray dried base beads the most important, of course, is the nonionic detergent. Although various nonionic detergents of
25 satisfactory physical characteristics may be utilized,

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including condensation products of ethylene oxide and propylene oxide with each other and with hydroxyl-containing bases, such as nonyl phenol and Oxo-type alcohols, it is highly preferred that the nonionic detergent be a condensation product of ethylene oxide and higher fatty alcohol.

In such products the higher fatty alcohol is of 10 to 20 carbon atoms, preferably 12 to 16 carbon atoms, and the nonionic detergent contains from about 3 to 20 ethylene oxide groups per mol, preferably from 6 to 12. Such detergents are made by Shell Chemical Company and are available under the trade names Neodol[®] 23-6.5 and 23-7.

The enzyme preparations, which normally are post-added to the base beads, may be any of a variety of commercially available products, included among which are Alcalase, manufactured by Novo Industri, A/S, and Maxatase, both of which are alkaline proteases (subtilisin). Although the alkaline proteases are preferred, amylotic enzymes, such as alpha-amylase, as well as proteolytic enzymes, may be utilized. The mentioned compositions usually contain active enzymes in combination with an inert powdered vehicle, such as sodium or calcium sulfate, and the proportion of active enzyme may vary widely, usually being from 2 to 80% of the commercial preparation. The perfumes employed, which are usually heat sensitive and may include some volatile solvent material, such as alcohol, are normally of synthetic

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perfumery materials, sometimes mixed with natural components, and generally will include alcohols, aldehydes, terpenes, fixatives and other normal perfume components. Flow promoting agents, such as special clays, which are sometimes added
5 to detergent products, while often useful to improve flowability and to diminish tackiness of various compositions, are unnecessary in the present case, possibly in part due to the presence of the bentonite. However, they may be added if desired, to further increase flowability.

10 The proportions of the various components in the base beads will be such as to result in their being free-flowing and sufficiently absorptive of a nonionic detergent applied thereto in liquid state so that the detergent composition made from them by incorporation of such detergent will
15 also be satisfactorily free-flowing. Also, of course, the detergent composition made from the base beads must be an effective cleaning agent, with the builders present acting to assist the organic detergent in aqueous solutions of the composition, and it is important that the resulting product
20 be one which does not cause objectionable deposition of zeolite particles (possibly with other substances) on washed materials. It has been found that satisfactory base beads to accomplish this purpose comprise, by weight, from 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 20
25 to 40% of water softening aluminum silicate (zeolite), 3 or 4 to

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12% of sodium silicate and 1 to 15% of bentonite, as the active components, and 1 to 15% of water. In such beads the aluminum silicate will preferably be a sodium zeolite containing from 15 to 25% by weight thereof of water of hydration and more preferably, such zeolite will be Zeolite A. The preferred weight ratio of sodium carbonate : sodium bicarbonate in the product is within the range of about 1 to 3, the beads made have a bulk density in the range of 0.6 to 0.9 g./cc., more preferably 0.7 to 0.8 g./cc. and the bead particle sizes are in the range of No's. 10 to 100 (through No. 10 and on No. 100), U.S. Sieve Series, more preferably 10 to 60, U.S. Sieve Series. Further preferred proportions of components are from 20 to 25% of sodium carbonate, 13 to 19% of sodium bicarbonate, 30 to 37% of hydrated zeolite, 5 to 8 or 10% of sodium silicate, 5 to 8% of bentonite and 4 to 10% of water, exclusive of the water of hydration of the zeolite. In such more preferred products the weight ratio of sodium carbonate : sodium bicarbonate is within the range of 1 to 2.

When a polyacrylate is present in the base bead composition the proportion thereof will normally be in the range of 0.1 to 2%, preferably 0.2 to 1.6% and more preferably 0.8 to 1.4%. Proportions of adjuvants and processing aids and fillers, if any, in the base beads, will normally be limited to 20% thereof, preferably being 1 to 10% and more preferably being 3 to 7% thereof. The proportions of processing aids, when magnesium sulfate and citric acid are

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employed, will normally be from 1 to 3% of magnesium sulfate, more preferably 1.5 to 2.5% thereof, and 0.2 to 1% of sodium citrate, more preferably 0.2 to 0.5% thereof. With respect to pigmenting and fluorescent brightening agents the proportions will preferably be from 0.05 to 0.6% of pigment, such as ultramarine blue, more preferably 0.2 to 0.4%, and 0.1 to 4% of fluorescent brightener, more preferably 1 to 3% thereof.

The ranges of proportions of the various bead components in the final detergent composition may readily be calculated from those given for the base beads, diminished by proportions of detergent and other materials post-added to the beads. Thus, if the final detergent composition had only nonionic detergent added to it so that the final product contains 20% of nonionic detergent, from the various ranges given for components in the base beads ranges of proportions thereof may be calculated by multiplying by 0.8, which is $(100 - 20)/100$. Similarly, when the proportion of nonionic detergent (in formulas wherein it is the only additive to the beads) may range from 8 to 25% of the detergent composition, the multipliers will be from 0.75 to 0.92. Usually the final percentage of nonionic detergent in the product will be in the 8 to 25% range, preferably being 15 to 22% and more preferably being about 20%, but in some situations, for certain types of products, proportions in the 8 to 13% range may be preferred. Normally the percentage

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of perfume in the final product will be in the range of 0.1 to 1%, preferably 0.2 to 0.4%, the percentage of enzyme will be from 0.5 to 3%, more preferably 1.5 to 2.5% and the percentage of flow improving agent, which may be post-added, will be less than 2%, preferably less than 1%. Of course, to calculate the ranges of bead components in the final composition, in addition to basing such calculations on the percentage of nonionic detergent in the final product (post-added) the percentages of other post-adjuvants will also have to be considered. Also, if some post-additions are made by means of aqueous solutions of the additives, this will affect the moisture content too, but such should be kept in the 1 to 12% range, which sometimes may be extended to 15%.

The base beads of the invention are spray dried from an aqueous crutcher mix which normally will contain from about 40 to about 70% of solids, preferably 50 to 65% thereof, with the balance being water, preferably deionized water as previously described, but city water may also be employed. The crutcher mix composition ranges may be calculated back from the desired base beads composition ranges on the basis of the moisture contents of the beads and the mix. Thus, for example, in a crutcher mix to contain 50% of moisture, from which mix a base bead containing 5% moisture is to be produced (neglecting water of hydration in the zeolite), the percentages of components in the base

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bead should be multiplied by 10/19, which is $(100/2[100 - 5])$.
The above calculations are satisfactory for components which
do not decompose in the spray drying operation but it is
known that a portion of the bicarbonate changes to carbonate
5 when dried at elevated temperatures in a spray tower.
Accordingly, knowing the characteristics of the tower and
the drying conditions, so that the extent of bicarbonate
decomposition is predictable, one can calculate the propor-
tion of carbonate and bicarbonate to have in the crutcher
10 mix. Thus, for example, when it is desired to make a
product containing about 22% of sodium carbonate and about
16% of sodium bicarbonate, in those cases wherein about
one-third of the bicarbonate decomposes to carbonate in the
spray tower (with two parts of carbonate resulting from three
15 parts of decomposed bicarbonate), one might charge 24%
bicarbonate and 17% of carbonate.

The crutcher mix from which the base beads of the
present invention are most preferably made by spray drying
is one which is primarily inorganic and/the content of
20 organic material is usually limited to 10%, preferably 7%,
and more preferably, to 4%, on a solids basis. Among such
organic materials which may be present are citric materials
(citric acid and soluble citrates), fluorescent brightener/
polyacrylate, dyes and pigments. Other organic materials
25 may also be present, including hydrotropic salts, chelating
agents and polyelectrolytes, but, as is evident, the crutcher
mix will remain primarily of inorganic materials and water.

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The crutcher mix is preferably made by sequentially adding various components thereof in the manner which will result in the most miscible, readily pumpable and non-setting slurry for spray drying. The order of addition of the

5 various components may be varied, depending on the circumstances, but it is highly desirable to add the silicate solution last, and if not last, at least after the addition of any gel or set preventing combination of materials or processing aids, such as citric acid and magnesium sulfate. Normally it is prefer-

10 able for all or almost all of the water to be added to the crutcher first, preferably at about the processing temperature, after which the processing aids and other minor components, including pigments and fluorescent brighteners (and poly-

15 acrylates, if present) are added, followed by the bentonite, zeolite, bicarbonate, carbonate and silicate. Usually during such additions each component will be mixed in thoroughly before addition of the next component but methods of addition may be varied, depending on the circumstances, so as to allow co-additions when such are feasible. Some-

20 times component additions, such as silicate additions, may be in two or more parts. For example, part of the silicate solution may be admixed with the other components of the mix before the carbonate and part afterward. Different components may sometimes be pre-mixed before addition, to

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speed the mixing process. Normally, mixing speed and power will be increased as the materials are added. For example, low speeds may be used until after admixing in of the last of the bentonite or zeolite, after which the speed may be
5 increased to medium and then to high before, during and after addition of the silicate solution.

The temperature of the aqueous medium in the crutcher will usually be about room temperature or elevated, normally being in the 20 to 70°C. range, and often preferably
10 will be from 25 to 40°C. Heating the crutcher medium may promote solution of the water soluble salts of the mix and thereby increase miscibility but the heating operation, when effected in the crutcher, can slow production rates. Therefore, an advantage of having the processing aiding materials
15 present in the mix is that at lower temperatures non-gelling slurries are obtainable. Temperatures higher than 70°C. will usually be avoided because of the possibility of decomposition of one or more crutcher mix components, e.g., sodium bicarbonate. Also, in some cases, lower crutcher
20 temperatures increase the upper limits of crutcher solids contents, probably due to insolubilizing normally gelling or setting components.

Crutcher mixing times to obtain good slurries can vary widely, from as little as ten minutes in small crutchers
25 and for slurries of higher moisture contents, to as much as four hours, in some cases. The mixing times needed to bring

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all the crutcher mix components substantially homogeneously together in one medium may be as little as five minutes but in some cases can take up to an hour, although 30 minutes is a preferable upper limit. Counting any such initial admixing
5 times, normal crutching periods will be from 15 minutes to two hours, e.g., 20 minutes to one hour, but the crutcher mix will be such as to be mobile, not gelled or set, for at least one hour, preferably for two hours, and more preferably for four hours or longer after completion of the making of
10 the mix, e.g., 10 to 30 hours before pump-out to the spray tower, for situations wherein other manufacturing problems may be encountered.

The crutched slurry, with the various salts and any other components thereof dissolved or in particulate
15 form, uniformly distributed therein, in part due to the desirable anti-gelling effects of the citric compound and the magnesium sulfate, and possibly also because of the polyacrylate, when present, is transferred in usual manner to a spray drying tower, which is located near the crutcher.
20 The slurry is normally dropped from the bottom of the crutcher to a positive displacement pump, which forces it at high pressure through spray nozzles at the top of a conventional spray tower (countercurrent or concurrent), wherein the droplets of the slurry fall through a hot drying gas,
25 usually the combustion products of fuel oil or natural gas, in which the droplets are dried to desired absorptive bead

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form. During the drying, part of the bicarbonate (often 1/4 to 1/2, e.g., 1/3) may be converted to carbonate, with the release of carbon dioxide, which appears to improve the physical characteristics of the beads made, so that they become more absorptive of liquids, such as liquid nonionic detergent, which may be post-sprayed onto them subsequently. However, the zeolite and bentonite components of the base beads made also appear to favor absorption of liquid, and the polyacrylate, when present, also helps to modify bead structure to promote absorption of liquid, so even with a lesser extent of decomposition of bicarbonate, a highly absorptive product still results.

After drying, the product is screened to desired size, e.g., 10 to 100 mesh, U.S. Sieve Series, and is ready for application of nonionic detergent spray thereto, with the beads being either in warm or cooled (to room temperature) condition. However, the nonionic detergent will usually be at an elevated temperature to assure that it will be liquid; yet, upon cooling to room temperature, desirably it will be a solid, often resembling a waxy solid. Even if at room temperature the detergent is somewhat tacky this characteristic does not make the final composition poorly flowing because the detergent penetrates to below the bead surface. The nonionic detergent, applied to the tumbling beads in known manner, as a spray or as droplets, is preferably a condensation product of ethylene oxide and higher

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fatty alcohol, such as was previously described, but other nonionics may also be operative.

The spray dried base beads and the detergent compositions made from them preferably include reduced proportions of silicate, preferably with the silicate content of the base beads being in the range of 5 to 10%, more preferably 5 to 8%, e.g., about 7%, and with the silicate contents and ranges of the final detergent composition being modified accordingly. Although, without the bentonite being present, more silicate, and in many cases, as much as twice or three times the proportion, e.g., 15% of the base beads, might be utilized, it is found that the present detergent compositions do not corrode aluminum articles and it appears that the amount of silicate present has a sufficient anti-corrosion effect in these compositions. Furthermore, the bentonite does not adversely affect the stability of the product and in fact, appears to help to hold the beads together. The presence of the bentonite significantly improves the properties of the final detergent composition, resulting in better calcium ion binding rates and in less zeolite being deposited on a laundered fabric. When the low molecular weight polyacrylate is present the beads become more porous and better absorb the nonionic detergent in liquid state, without unduly lowering the bulk density of the product. Considering that bentonite is a clay and might be expected to create deposition problems of its own, the

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lowered deposition of zeolite is surprising and constitutes a significant part of the present invention.

It is noted that the employment of low molecular weight polyacrylate in zeolite-carbonate-bicarbonate-silicate base beads for the manufacture of nonionic detergent compositions is not a part of the present invention because such was invented by co-workers of the present applicant (and is the subject of a separate co-pending U.S. patent application). However, it has been found that such polyacrylate improves the properties of the present invented compositions too, and therefore such further improved products are disclosed and claimed herein.

The following examples illustrate but do not limit the invention. Unless otherwise indicated all temperatures are in °C. and all parts are by weight in the examples and throughout the specification. Also, when weights and proportions of zeolite are given these are intended to be for the normal hydrate being used, because it is considered that the zeolite water of hydration does not leave the zeolite and does not become part of the aqueous solvent medium in the present crutching operations./

EXAMPLE 1

A 10,000 pound (4,536 kg.) batch of crutcher mix for spray drying to base beads of this invention and conversion to a detergent composition is made by adding to the

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crutcher 4,038 lbs. of deionized water at a temperature of about 27°C. (80°F.), and sequentially and with low speed crutcher mixing, admixing with it 113 lbs. of anhydrous magnesium sulfate (232.6 lbs. of epsom salts may be used instead, in which situation the water charged initially will be reduced to 3918.4 lbs.), 28 lbs. of citric acid, 127 lbs. of Tinopal 5BM Extra Conc. (CIBA-Geigy), 15 lbs. of ultramarine blue powder, 374 lbs. of Thixo-Jel No. 1 (bentonite), 2,015 lbs. of Linde hydrated Zeolite 4A (20% water of crystallization), 1,404 lbs. of sodium bicarbonate and 1,006 lbs. of sodium carbonate (soda ash). The mixer speed is then increased to high (in some cases it may be increased to medium speed at an earlier time if the mix is not blending as well as desired) and 418 lbs. of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4) are admixed (as 880 lbs. of a 47.5% of aqueous solution). Mixing of the entire batch then continues for about an hour (in some cases as long as four hours mixing may be used), during which time about 200 to 600 lbs. of water may be lost by evaporation, which water may be replenished if desired. During the mixing time the crutcher slurry is continuously mobile and does not gel, set or cake. Because bicarbonate partially decomposes to carbonate during spray drying, the amounts thereof may be varied, depending on the spray tower operating characteristics.

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Starting about five minutes after all the components of the crutcher mix are present, the mix is dropped from the crutcher to a pump, which pumps it at a pressure of about 300 p.s.i. (about 21 kg./sq. cm.) into the top of a counter-
5 current spray tower wherein the initial temperature is about 800°F. (430°C.) and the final temperature is about 220°F. (105°C.). The essentially inorganic base beads resulting are of a bulk density of about 0.6 to 0.7 g./ml., an initial
10 adhesion approximating 40%, of particle size range substantially between 10 and 100 mesh, U.S. Sieve Series (they are screened to such range), and of a fines characteristic (through U.S. Sieve No. 50) of about 15%. The moisture content of the beads is about 7%. The base beads are found to be free-flowing, non-tacky, satisfactorily porous, yet
15 firm on the surfaces thereof, and are capable of readily absorbing significant proportions of liquid nonionic detergent without becoming objectionably tacky.

Detergent products are made from the spray dried beads by spraying onto the tumbling bead surfaces thereof a
20 normally waxy nonionic detergent, either Neodol 23-6.5 or Neodol 23-7, in heated liquid state, in such quantity as to result in a final product containing 20% of nonionic detergent, and proteolytic enzyme (Alcalase) is applied in powdered form to result in a 1.99% concentration in the product.
25 Perfume is sprayed onto the product to produce a 0.25% concentration therein. The resulting detergent products are of

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a bulk density of about 0.7 or 0.8 g./ml. and contain 27.3% of zeolite (hydrated), 20.1% of the nonionic detergent, 17.8% of sodium carbonate (some of which is produced by decomposition of sodium bicarbonate), 12.7% of sodium bicarbonate, 5.6% of sodium silicate, 5.45% of water, 2.0% of enzyme, 1.7% of fluorescent brightener, 1.5% of magnesium sulfate, 0.4% of citric acid (in citrate form), 0.25% of perfume, 0.2% of ultramarine blue, and 5.0% of bentonite (Thixo-Jel). The detergent made, of the above formula, is an excellent heavy duty laundry detergent and is especially useful for washing household laundry in automatic washing machines. It is physically and aesthetically advantageous and attractive because it is non-dusting and extremely freely flowing, which allows it to be packaged in narrow-necked glass and plastic bottles, from which it flows readily for dispensing. The detergent compositions of the invention, containing bentonite, as described, are found to be of significantly improved calcium ion binding rates but more importantly, they leave less residue on laundry washed with them (in an automatic washing machine at usual concentrations for such product and at normal wash temperatures) than do similar compositions not containing the bentonite. This difference is accentuated when the wash water is high in hardness, e.g., 200 p.p.m., as calcium carbonate, the wash water is cold, and a gentle agitation cycle is employed.

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In a control experiment base beads are made in which the bentonite is omitted from the crutcher mix, being replaced by equal weights of sodium carbonate and sodium bicarbonate, the total of the added materials equalling the weight of the bentonite replaced. The crutcher mix is spray dried and converted to a detergent composition in the same way used to make the invented detergent composition. Such "control" product, while useful as a detergent, results in more residue being deposited on washed/laundry than with the experimental product of this invention and is of a lower calcium binding rate. Similarly, when the content of silicate in the control beads is increased to 10.7%, with sodium carbonate and sodium bicarbonate concentrations being decreased to compensate for the silicate increase, the residue deposition is even worse than with the control.

Following normal procedure, crutcher mixes will be made quickly and may be emptied from the crutcher equally fast, sometimes being made within a period of as little as five minutes and being pumped out of the crutcher in as little as ten minutes. Yet, it is often important that the present mixes be able to withstand at least an hour in the crutcher without gelling or solidifying because sometimes holdups of such times are encountered in commercial production. The described crutcher mix is capable of being held for as long as four hours, and often appreciably longer, without

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gelling or solidifying, which is attributed, at least in part, to the content of magnesium sulfate and citric acid processing aids therein. However, other processing aids intended to prevent gelation and setting of the crutcher mixes may be substituted, and under some conditions the proportions thereof may be decreased and one or both may be omitted. Similarly, other minor components of the crutcher mix, such as the fluorescent brightener and pigment may be omitted therefrom and enzyme and perfume may be omitted from the final product, although it is highly preferable for all such materials to be present. The crutcher mix temperature may be modified, as by elevation to 52°C., and the proportions of the various components may be varied $\pm 10\%$, $\pm 20\%$ and $\pm 30\%$, while still maintaining them within the ranges previously given, and workable crutcher mixes that result in the desired beads and detergent compositions will be obtainable.

Instead of employing anhydrous magnesium sulfate an equivalent proportion of epsom salts may be substituted and various other components may be added as aqueous solutions, providing that the amounts of moisture added with them are subtracted from that added to the crutcher. Other orders of addition may be employed but normally it will be desired to have the processing aids added early in the manufacturing procedure, with the silicate being added last or near the end thereof. Instead of using Zeolite 4A, Zeolites X and Y

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may be substituted, as may be other types of Zeolite A. While it is preferred to employ the hydrated Zeolite 4A of this example, various degrees of hydration of the zeolite are acceptable and in some instances nearly anhydrous crystalline zeolites or amorphous zeolites may be employed. Varying the amount of bentonite within the range given, to 3% and 10%, for example, still results in useful products but those containing larger proportions of bentonite will usually be more effective in preventing zeolite deposition on laundry. However, the proportion employed commercially depends on a number of factors and normally will represent a balance struck between the desired diminution of zeolite residue and the desired building and other functional effects of other detergent composition components.

15 EXAMPLE 2

A product like that of Example 1 is made but with the addition of low molecular weight polyacrylate (MW = 1,000 to 2,000) in the crutcher mix, added early in the production thereof, before the bentonite, so as to result in a comparable product containing 1% of the polyacrylate (Alcosperse 107D). The only formula change to compensate for the addition of the polyacrylate is a decrease in the sodium bicarbonate content in the crutcher mix by an equal weight. Additionally, the batch made is smaller, using a pilot plant crutcher. The base beads resulting from spray

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drying, which is effected in the same manner as previously described in Example 1, are converted to a final detergent product of the same type as in Example 1, with the exception of the addition of the polyacrylate. The composition is
5 tested and the properties thereof are observed. It is found to be an excellent free flowing detergent, with less zeolite residue on washed laundry than controls of the types mentioned in Example 1. Additionally, the presence of the Alcosperse noticeably improves the absorption characteristics of the
10 beads made so that they more readily absorb liquid nonionic detergent, which may be of the ethoxylated alcohol type or other types mentioned in the specification. Yet, the bulk densities of the beads and the product are not lowered appreciably, which is significant when it is desired to
15 manufacture a comparatively high bulk density, concentrated particulate detergent. It has been observed that when the described polyacrylate is present in the crutcher mix better spray drying operations result and less material is lost by deposition on the spray tower walls, which processing
20 advantages are important in speeding commercial production and in avoiding waste and reworking of off-grade material.

As with Example 1, the proportions of components in this example may also be varied, within the limits given in the specification, to produce base beads and detergent
25 compositions of improved properties. While it appears that

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about 1% of the described polyacrylate is an optimum proportion to utilize in the detergent compositions, from 0.1 to 2% thereof will have good effects, with use of the greater proportions resulting in greater porosity improvements of the beads. For example, instead of 1%, 0.5% and 1.5% are also desirable proportions of the polyacrylate. In some cases it may be desirable to utilize polyacrylates of higher molecular weights within the ranges given, e.g., 4,000-5,000, but in most cases the lower portion of the range will be preferred. As with Example 1, in some instances processing aids, perfume, enzyme, fluorescent brightener and pigment may be omitted or changed but in all instances the mentioned zeolite, carbonate, bicarbonate, silicate and bentonite will be present in the given proportions in the base beads, and nonionic detergent will also be present in the final detergent composition, which, like the others, is of the non-phosphate type.

The invention has been described with respect to various examples and illustrations thereof but is not to be limited to these because it is clear that one of skill in the art, with the present description before him, will be able to utilize substitutes and equivalents without departing from the invention.

WHAT IS CLAIMED IS:

1. Free flowing base beads, useful, by application of nonionic detergent thereto, for manufacture of particulate built synthetic nonionic organic detergent products of improved washing properties, comprising by weight from 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 20 to 40% of a water softening hydrate zeolite which has an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalent of calcium carbonate hardness per gram of anhydrous zeolite swelling bentonite.

2. Beads according to Claim 1, of a bulk density of 0.6 to 0.9 g./cc. and particles sizes in the range of No. 10 to 100, U.S. Sieve Series, wherein the water softening sodium zeolite containing from 15 to 25% by weight thereof water of hydration and has an exchange capacity for calcium ions which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.4 to 1:3 and the weight ratio of sodium carbonate : sodium bicarbonate is within the range of about 1 to 3.

3. Beads according to Claim 2 comprising
from 20 to 25% of sodium carbonate, 13 to 19% of
sodium bicarbonate, 30 to 37% of hydrated zeolite,
5 to 8% of sodium silicate, 5 to 8% of bentonite and
4 to 10% of water, exclusive of the water of hydra-
tion of the zeolite, and in which the zeolite is
Zeolite A, of ultimate mean particle sizes in the
range of 3 to 12 microns, of a calcium ion exchange
capacity of 250 to 350 mg. eq./g. and of a hardness
depletion rate residual hardness less than 0.01 mg./
l. in ten minutes, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$
ratio in the range of 1:2 to 1:2.4, the bentonite is
a swelling clay having a swelling capacity, in water,
of 3 to 15 ml./gram and a viscosity of 3 to 30 centi-
poises at 6% concentration in water, and the weight
ratio of sodium carbonate : sodium bicarbonate is
within the range of 1 to 2.

4. Beads according to Claim 3 wherein the
bentonite is beneficiated Wyoming bentonite of swell-
ing capacity in the range of 7 to 15 ml. and of vis-
cosity in the range of 8 to 30 cp. at 6% concentra-
in in water.

5. Beads according to Claim 4 which further
comprises from 0.05 to 0.6% of ultramarine blue, 0.1
to 4% of a fluorescent brightening agent, 1 to 3% of
magnesium sulfate and 0.2 to 1% of sodium citrate.

6. Beads according to Claim 5 which are of a bulk density of 0.6 to 0.8 g./cc., and comprise 0.2 to 0.4% of ultramarine blue, 1 to 3% of fluorescent brightening agent, 1.5 to 2.5% of magnesium sulfate and 0.2 to 0.5% of sodium citrate.

7. Beads according to Claim 1 which further comprises from 0.1 to 2% of polyacrylate of molecular weight in the range of 1,000 to 5,000.

8. Beads according to Claim 7 in which the polyacrylate is a sodium polyacrylate of molecular weight in the range of 1,000 to 3,000 and the percentage thereof present is in the range of 0.8 to 1.4%.

9. Beads according to Claim 4 which further comprises from 0.1 to 2% of polyacrylate of molecular weight in the range of 1,000 to 5,000.

10. In a detergent composition which includes nonionic synthetic organic detergent, sodium carbonate, sodium bicarbonate, water softening zeolite, and bentonite, the improvement which comprises base beads according to Claim 1 with 8 to 25%, on a final composition basis, of nonionic synthetic organic detergent absorbed therein.

11. A detergent composition according to

5 Claim 10 wherein the nonionic detergent is a condensation product of 6 to 12 moles of ethylene oxide and a higher fatty alcohol of 12 to 16 carbon atoms and which detergent composition also comprises from 0.5 to 3% of an enzyme and 0.1 to 1% of perfume.

10 12. In a detergent composition which includes nonionic synthetic organic detergent, sodium carbonate, sodium bicarbonate, water softening zeolite, sodium silicate and bentonite, the improvement which comprises base beads according to Claim 7 with 8 to 25%, on a final composition basis, of nonionic synthetic organic detergent absorbed therein.

15 13. A detergent composition which comprises beads in accordance with Claim 8 having absorbed in them a nonionic detergent so that the percentage of such nonionic detergent in the detergent composition is within the range of 15 to 22%.

20 14. A detergent composition according to Claim 13 wherein the nonionic detergent is a condensation product of 6 to 12 moles of ethylene oxide and a higher fatty alcohol of 12 to 16 carbon atoms, and which detergent composition also comprises from 0.5 to 3% of an enzyme and 0.1 to 1% of perfume.

15. A process for manufacturing base beads which are useful for the manufacture of particulate built synthetic nonionic organic detergent compositions, which comprises mixing together an aqueous mixture of sodium carbonate, sodium bicarbonate, water softening zeolite, sodium silicate and bentonite, which contains 40 to 70% of the mentioned components and 60 to 30% of water and is at a temperature in the range of 40 to 70°C., and spray drying the aqueous mixture in a spray drying tower with air at an elevated temperature, which decomposes a portion of the bicarbonate to carbonate, so as to produce base beads which contain 15 to 30% of sodium carbonate, 10 to 22% of sodium bicarbonate, 20 to 40% of water softening zeolite and 1 to 15% of bentonite.

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