

- [54] Title: SPRAY DRIED BASE BEADS AND DETERGENT COMPOSITIONS
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U. S. A.
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4,264,464	4/1981
4,325,829	4/1982
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A B S T R A C T

Free flowing, spray dried beads which are useful as a detergent or for the manufacture of a particulate built synthetic nonionic organic detergent composition include water softening aluminosilicate (such as a zeolite), bentonite and water soluble builder, and may also include water soluble synthetic organic detergent and a small proportion of water soluble silicate, although such silicate is preferably omitted. The beads can be made to be of a bulk density within a broad range, and the bulk density may be varied by control of the bead formula and by modification of spray drying conditions. The base beads and detergent compositions formulated with them are of reduced aluminosilicate deposition characteristics, due to the presence of bentonite and the absence of or presence of only a low content of water soluble silicate, with the bead composition being maintained within given ranges. The moisture content of the beads will be such as to maintain at least 2% and preferably 3% or 4% or more of moisture in the bentonite so that its normal swelling power is retained, because the

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welling of the bentonite is considered to be important in dispersing the beads in wash water and also, even more importantly, in helping to prevent aluminosilicate agglomeration and objectionable deposition thereof on materials washed, and in helping to break up any minor proportion of such agglomerates which might be formed.

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SPRAY DRIED BASE BEADS AND DETERGENT

COMPOSITIONS

ABSTRACT OF THE DISCLOSURE:

Free flowing, spray dried beads which are useful as a detergent or for the manufacture of a particulate built synthetic nonionic organic detergent composition include water softening aluminosilicate (such as a zeolite), bentonite and water soluble builder, and may also include water soluble synthetic organic detergent and a small proportion of water soluble silicate, although such silicate is preferably omitted. The beads can be made to be of a bulk density within a broad range, and the bulk density may be varied by control of the bead formula and by modification of spray drying conditions. The base beads and detergent compositions formulated with them are of reduced aluminosilicate deposition characteristics, due to the presence of bentonite and the absence of or presence of only a low content of water soluble silicate, with the bead composition being maintained within given ranges. The moisture content of the beads will be such as to maintain at least 2% and preferably 3% or 4% or more of moisture in the bentonite so that its normal swelling power is retained, because the swelling of the bentonite is considered to be important

in dispersing the beads in wash water and also, even more importantly, in helping to prevent aluminosilicate agglomeration and objectionable deposition thereof on materials washed, and in helping to break up any minor proportion of such agglomerates which might be formed.

pentasodium tripolyphosphate, which had been used to
a great extent in built laundry detergent compositions,
had been suspected in some quarters of being harmful,
and accordingly, for years compositions containing BTA
5 were not marketed in the United States. There has never
been any serious doubt that phosphates are safe for
humans and recently disapproval by United States authorities
of the use of NTA in detergents has been withdrawn.
Accordingly, although certain non-phosphate detergent
10 formulations will continue to be manufactured for
employment in areas that are located adjacent to lakes
and rivers, wherein the phosphate tends to provide a
needed nutrient for algae growth and thereby may cause
some eutrophication of such waters, detergent compositions
15 containing phosphate and/or NTA are marketable once
more.

Although the zeolites, preferably Zeolite A and
especially preferably hydrated Zeolite 4A, had been
builder salts in phosphate-free and NTA-free detergent
20 compositions, they have now also been found to be useful
components of improved detergent and base bead compositions
containing phosphat(s) and/or NTA. Normally about 6 to
12% of water soluble sodium silicate has been utilized
in crutcher mixes from which spray dried base beads or
25 detergent compositions were to be made. The silicate has

5 This invention relates to free flowing, spray
dried base beads which are useful for the manufacture
of a particulate built synthetic nonionic organic de-
tergent composition. It also relates to free flow-
ing, spray dried detergent compositions. More parti-
cularly, the invention relates to such beads and com-
positions which contain certain proportions (within
prescribed ranges) of a water softening aluminosili-
cate, such as a zeolite, bentonite, and water soluble
10 builder for detergents. The product made is of reduced
zeolite deposition characteristics compared to prior
art products containing similar proportions of the wa-
ter softening aluminosilicate. Such prior art products
would normally also have contained appreciable propor-
15 tions of water soluble silicate and usually would not
have contained bentonite.

In recent years water softening insoluble alumi-
nosilicates, such as hydrated zeolites, have been em-
ployed as builder constituents in laundry detergent com-
20 positions. Initially, renewed interest in the zeolites
appears to have been stimulated by the necessity of pro-
ducing detergent formulations which did not contain phos-
phates. Trisodium nitrilotriacetate and other salts of
nitrilotriacetate acid (NTA), which had been suggested as
25 potential replacements for the phosphates, especially for

been employed for its binding effect on the other components of the beads, which binding results in stable beads, and it has been discovered to help to produce a reticulated inner bead structure. It also functions as an anti-corrosion additive which prevents chemical attack on aluminum parts of washing machines and other appliances with which the detergent solution may come into contact. However, in proportions formerly employed, e.g., 8 to 10% in the finished product, it had been noted that the combination of the water soluble silicate and the zeolite in the crutcher led to the production of aggregates of such materials in the spray dried beads, which aggregates objectionably deposited on washed materials, tending to adversely affect the appearances of colors thereof. By means of the present invention, utilizing certain proportions of zeolite, bentonite and water soluble builder, with little or no water soluble silicate, spray dried beads of sufficient mechanical stability to be commercially acceptable result and these are of reduced zeolite deposition characteristics (or reduced zeolite-silicate aggregate deposition characteristics). Even when a small proportion of silicate is present it appears that the bentonite helps to counteract any tendency of the zeolite and silicate to react to produce a par-

ticle of larger size than that of the zeolite normally present, and thereby undesirable deposition of zeolite or zeolite-silicate particles on washed fabrics is prevented or lessened. Additionally, the compositions containing bentonite are much more readily disintegrated and distributed throughout the wash water, again apparently due to the presence of bentonite therein. Another advantage of the invention, when little or no silicate is employed, is that formulations containing carbonate and/or bicarbonate do not require the presence of anti-gelling materials to prevent excessive thickening of the crutcher mix. Such additives are not usually necessary when the principal builder of the detergent is a phosphate and when little or no carbonate and/or bicarbonate are present, but for non-phosphate compositions, which often will contain appreciable quantities of carbonate and/or bicarbonate, the omission of anti-gelling materials is decidedly advantageous, with respect to both processing and from an economic standpoint.

The prior art relating to detergent compositions, softening compositions and detergent softener compositions includes teachings that various detergent compositions can be made containing one or more of zeolite, bentonite, silicate, phosphate, NTA, quaternary ammonium compounds (softeners), and other components, usually

with synthetic organic detergent, but although the disclosure contain extensive recitations (sometimes referred to as "laundry lists") of almost all materials which have been employed for any purpose in detergent and softener compositions, they do not include clear teachings or suggestions of the detergent compositions of the present invention, and this is especially true with respect to those compositions containing little or no soluble silicate. The disclosure do not appear to recognize the importance of the bentonite containing sufficient "lubricating" water between the plates thereof, and they do not appreciate the combination of binding and disintegrating effects attributable to the "hydrated" bentonite. Also, many of the "reference" formulas contain appreciable proportions of sodium sulfate, a filler, possibly to improve the physical properties of the product particles, but such is not needed to make the invented compositions, which therefore can be of greater active ingredients (including builder) contents.

In accordance with the present invention free-flowing, spray dried beads, useful as a detergent or for the manufacture of a particulate built synthetic nonionic organic detergent composition, which detergents are of reduced particle deposition characteristics due to the presence of bentonite and a low content of water solu-

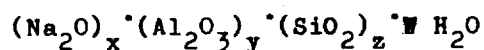
ble silicate or absence of such silicate in the spray
dried beads, comprise by weight from 5 to 60% water of
softening aluminosilicate, 2 to 40% of bentonite, con-
taining sufficient moisture to facilitate dispersion
5 of the bentonite so as inhibit deposition of aluminosili-
cate on laundry being washed, 5 to 60% of water soluble
builder or a mixture of such builders, 0 to 30% of water
soluble synthetic organic detergent and 0 to 5% of water
soluble silicate. The aluminosilicate may be a zeolite
10 having a substantial exchange capacity for calcium ion,
the bentonite is of appreciable swelling capacity in wa-
ter and includes a sufficient proportion of moisture to
facilitate disintegration of the plate-to-plate bonds there-
of when the detergent beads, alone or in mixture with other
15 detergent components, are placed in water, the water soluble
builder or builder mixture is a polyphosphate, nitrilotri-
acetate or carbonate, and there is no water soluble sili-
cate present. Also within the invention are detergent com-
positions made by spray drying the described bead formula
20 with an anionic detergent present in the crutcher mix or
by the spraying nonionic detergent in liquid form onto tumb-
ling detergent-free beads or beads containing only rela-
tively small proportions of anionic detergent or mixture
of anionic detergents. Mixtures of such compositions, mix-
25 ed anionic and nonionic detergent compositions, are also

useful and may possess superior washing properties.

5 The zeolites employed include crystalline, amorphous and mixed crystalline-amorphous zeolites, of both natural and synthetic origins, which 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 10 the wash water before adverse reactions of such ions with other components of the synthetic organic detergents composition occur. The zeolites employed may be characterized as having a high exchange capacity for 15 calcium ion, which is normally from about 200 to 400 or more milligram equivalent 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 harness of 0.02 to 0.05 mg. 20 CaCO_3 /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.

25 Although other ion exchanging zeolites may also be utilized, normally the finely divided synthetic zeolite builder particles employed in the practice of this invent-

ion will be of the formula



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-ex-
changing zeolite, i.e., it should be an aluminosili-
cate of a univalent cation such as sodium, potassium,
lithium (when practicable) or other alkali metal, am-
monium or hydrogen (sometime). Preferably the univalent
cation of the zeolite molecular sieve is an alkali me-
tal cation, especially sodium or potassium, and not
most preferably it is sodium.

Crystalline types of zeolites utilizable as good
ion exchangers in the invention, at least in part, in-
clude zeolites of the following crystals structure groups
A, X, Y, L, mordenite and erionite, of which types A, X
and Y are preferred. Mixtures of such molecular sieve
zeolites can also be useful, especially when type A zeo-
lite is present. These crystalline types of zeolites
are well known in the art and more particularly des-
cribed in the text Zeolite Molecular Sieves, by Donald
W. Breck, published in 1974 by John Wiley & Sons. Typi-
cal commercially available zeolites of the aforementioned
structural types are listed in Table 9.6 at pages 747-

749 of the Breck text. Such zeolites are known in the art. Some, and other such suitable zeolites have been described in many patents in recent years for use as detergent composition builders.

5 The zeolite used in the invention is usually synthetic and it is often characterized by 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, and such zeolites are preferred. Such zeolite molecular sieves are described in U.S. patent 2,882,243, which refers to them as Zeolite A.

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20 Molecular sieve zeolites of ion exchanging and water softening properties can be prepared in either a dehydrated or calculated 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

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zeolite total weight, depending on the type of zeolite used. The water containing hydrated for of the molecular sieve zeolite (preferably hydrated to about 15 to 70% of capacity) is preferred in the practice of this invention when a crystalline product is to be used. The manufacture of such crystal 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 a a hydrous amorphous sodium aluminosilicate gel) are used without undergoing high temperature dehydration (calcining to 3% or less water content) that is normally practiced in preparing such crystals for use as catalyst, 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%, preferably about 10 or 15% to 25%, such as 17 to 22%, e.g., 20%. However, the moisture content of the molecular sieve type zeolite being employed may be lower, as we previously described, in which case the zeolite can be hydrated during crutch-
ing 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, more preferably being from 0.01 to 15 microns, e.g., 3 to 12 microns, and especially preferably being of 0.01 to 8 microns mean particle size, e.g., 3 to 7 microns, if crystalline, and 0.01 to 0.1 microns, 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 attach to carbonate, bicarbonate, phosphate and/or NTA base particles nuclei on which they may be distributed with the bentonite, such as in a gel-like or film state, during spray drying of a crutcher mix to form 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 most 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 Mineral Colloid, as industrial bentonites, by Benton Clay Company, an affiliate of Georgia Kaolin Co. These materials which are the same as those formerly sold under the trademark THIXO-JEL, are selectively mined and beneficiated bentonite, and those considered to be most useful are available as Mineral Colloid No's. 101, etc., corresponding to THIXO-JELS No's. 1, 2, 3 and 4. Such materials have pH's (6% concentration in water) in the range of 8 to 9.4, maximum free moisture contents of about 8% and specific gravities of about 2.6, and for the pulverized grade about 85% passes through a 200 mesh U.S. Sieve Series sieve. Beneficiated Wyoming bentonite is preferred as a component of the present compositions but other ben-

tonites are also useful, especially when they form a minor proportion of the bentonite used. Although it is desirable to limit maximum free moisture content, as mentioned, it is even more important to make certain
5 that the bentonite being employed includes enough free moisture, most of which is considered to be present between adjacent plates of the bentonite, to facilitate quick disintegration of the bentonite and any adjacent materials in the particles when such particles or detergent compositions containing them are brought into
10 contact with water, such as wash water. It has been found that at least about 2%, preferably at least 3% and more preferably, about 4% or more of water should be present in the bentonite initially, before it is admixed with the
15 other bead components in the crutcher, and such proportion should also be present after spray drying. In other words, overdrying to the point where the bentonite loses its "internal" moisture can significantly diminish the utility of the present compositions. When the bentonite moisture content is too low the bentonite does not act to prevent silicate-zeolite agglomerates being formed and it also does
20 not aid in disintegrating the beads in the wash water. When the bentonite is of satisfactory moisture content it exhibits an exchangeable calcium oxide percentage in the
25 range of about 1 to 18 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 0.0% of K_2O .

The water soluble builder or mixture thereof employed may be one or more of the conventional materials that have been used as builders or suggested for such purpose. These include inorganic and organic builders, and mixtures thereof. Among the inorganic builders those of preference are the various phosphates, preferably polyphosphates, e.g., tripolyphosphates and pyrophosphates, such as pentasodium tripolyphosphate and tetrasodium pyrophosphate. Trisodium nitrilotriacetate (NTA), preferably employed as the monohydrate, and other nitrilotriacetates, such as disodium nitrilotriacetate, are preferred water soluble builders. Sodium tripolyphosphate, sodium pyrophosphate and NTA may be utilized in hydrated forms but even when anhydrous compounds are used the bentonite and zeolite appear to inhibit caking due to subsequent hydration. Of course, carbonates, such as sodium carbonate, are useful builders and may desirably be employed, alone or in conjunction with bicarbonates, such as sodium bicarbonate. When the polyphosphates are

employed it may be preferred to have sodium pyrophosphate present with sodium tripolyphosphate in proportion from 1:10 to 10:1, preferably 1:5 to 5:1 with respect to it, with the total proportion of both builders being about the same as that mentioned herein for the sodium tripolyphosphate. Other water soluble builders that are considered to be effective include the various other inorganic and organic phosphates, borates, e.g., borax, citrates, gluconates, EDTA and iminodiacetates. Preferably the various builders will be in the form of their alkali metals salts, either the sodium or potassium salts, or a mixture thereof, but sodium salts are normally more preferred. In some instances, as when neutral or slightly acidic detergent compositions are being produced, acid forms of the builders, especially of the organic builders, may be preferable but normally the salts will either be neutral or basic in nature. The silicates, preferably sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio within the range of 1:1.6 to 1:3.0, preferably 1:2 to 1:2.8, e.g., 1:2.35 or 1:2.4, also serve as builder salts but because of their strong binding properties and their characteristic of promoting aggregation or agglomeration with zeolite particles, they are special cases of builders and it is preferred that they be omitted from the present compositions. However, because they do possess anti-corrosion

properties, especially important when the detergent solution is to be employed in washing machines or other appliances in contact with aluminum parts thereof, they may sometimes be present in limited small proportions. In such instances it may be preferable for hydrated sodium silicate particles to be post-added, so that they do not react with or agglomerate with zeolite particles in the crutching and spray drying operations. Although sodium sulfate and sodium chloride and other filler salts possess no building properties they are sometimes utilized in detergent compositions for their filling characteristics. In addition to increasing the volume and weight of the product to facilitate measuring, they also sometimes improve bead stabilities and physical properties of the detergent composition beads in which they are incorporated. Nevertheless, because the present compositions are satisfactory without any fillers being present, such are preferably avoided entirely or any proportion thereof present is minimized, usually to a practical minimum.

Usually the detergent(s) employed will normally be either nonionic or anionic or both but amphoteric or ampholytic detergents may also be used, especially in conjunction with nonionics and/or anionics in the present compositions. Cationic detergents may serve as fabric softeners in these products but normally will not be

5 spray dried with anionic detergents, due to an undesirable interaction that can take place. These classes of materials are well known and have been described repeatedly in the detergent art. Because they are not preferred components of the present compositions no further description thereof in this specification is considered to be appropriate.

10 Although various nonionic detergents of satisfactory physical characteristics may be utilized, 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
15 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 or 30 ethylene oxide groups per mol, preferably from 6 to 12. Most preferably, the nonionic detergent will be one in which the higher fatty alcohol is
20 of about 12 to 13 or 15 carbon atoms and which contains from 6 to 7 or 11 mols of ethylene oxide. Such detergents are made by Shell Chemical Company and are available under the the trade names Neodol[®] 23-6.5 and 25.7.
25 Among their specifically attractive properties, in addition to good detergency with respect to oily marks on

goods to be washed, is a comparatively low melting point, yet appreciably above room temperature, so that they may be sprayed onto base beads as a liquid which solidifies.

5 Various anionic detergents, usually as sodium salts, may be employed but those which are most preferred are linear higher alkyl benzene sulfonates, higher alkyl sulfates and higher fatty alcohol polyethoxylate sulfates. Preferably, in the higher alkyl benzene sulfonate the higher alkyl is linear and of 10 12 to 15 carbon atoms, e.g., 13, and is a sodium salt. The alkyl sulfate is preferably a higher fatty alkyl sulfate of 10 to 18 carbon atoms, preferably 12 to 16 carbon atoms, e.g., 12, and is also employed as the sodium salt. The higher alkyl ethoxamer sulfates will 15 similarly be of 10 or 18 carbon atoms, e.g., 12, in the higher alkyl, which will preferably be a fatty alkyl, and the ethoxy content will normally be from 3 to 30 ethoxy groups per mol, preferably 3 or 5 to 20. Again, 20 the sodium salts are preferred. Thus, it will be seen that the alkyls are preferably linear or fatty higher alkyls of 10 to 18 carbon atoms, the cation is preferably sodium, and when a polyethoxy chain is present the sulfate is at the end thereof. Other useful anionic detergents include the higher olefin sulfonates and para- 25

5 ffin sulfonates, e.g., the sodium salts wherein the
olefin or paraffin groups are of 10 to 18 carbon atoms.
Specific examples of the preferred detergents are so-
dium tridecyl benzene sulfonate, sodium tallow alcohol
polyethoxy (3 EtO) sulfate, and sodium hydrogenated tal-
low alcohol sulfate. In addition to the preferred anio-
nic detergents mentioned, others of this well known group
may also be present, especially in only minor proportions
with respect to those previously described. Also, mixtures
10 thereof may be employed and in some cases such mixtures can
be superior to single detergents. The various anionic de-
tergents are well known in the art and are described at
length at pages 25 to 138 of the text Surface Active Agents
and Detergents, Vol. II, by Schwartz, Perry and Berch, pub-
15 lished in 1958 by Interscience Publishers, Inc.

20 Various adjuvants may be present in the crutcher
mix from which base beads or detergent compositions may
be spray dried, or such adjuvants may be post-added, with
the decision as to the mode of addition often being deter-
mined by the physical properties of the adjuvant, its re-
sistance to heat, its resistance to degradation in the
aqueous crutcher medium, and its volatility. Among the
more important of the adjuvants is a polycrylate which
has been found to be useful in controlling bead characte-
25 ristics and bulk density, has dispersing, anti-deposition

and anti- redeposition effects in the present compositions, and aids in maintaining the crutcher mix fluid and homogeneous.

5 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., about 1/2 or 1/3
10 present as sodium polyacrylate. 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 substitutions be limited to a minor
15 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
20 are available clear amber liquids or powders, with their solutions being of about 25 to 40% solids content, e.g., 30%, and with the pH of such solutions or of a 30% aqueous solutions of the powder being in the range of about 7.5 to 9.5, e.g., about 9. Such materials are
25 completely soluble in water and have been 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. In the present spray drying process small quantities (or percentages) thereof help to make the resulting beads of improved porosity.

When the crutcher mix includes carbonate and/or bicarbonate and silicate, even if the amount of the silicate is small, there may be a tendency for the mix to gel or "freeze" in the crutcher, especially if, due to delays in processing, the crutcher mix is held longer than the normal 30 minutes or so. In such cases, when silicate is present processing aids are preferably also present in the mix (and consequently, in the finished base beads and detergent composition) to prevent premature solidification or gelation. 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.
However, while such processing aids are useful in
many cases, it is a feature of this invention that
5 they are not needed in manufacturing the preferred
base beads from which silicate is omitted.

Although some adjuvants, such as fluorescent
brightener, pigment, e.g., ultramarine blue, titanium
dioxide, and inorganic filler salt may be added in the
10 crutcher, others, such as perfumes, enzymes, bleaches,
some colorants, bactericides, fungicides, fabric soft-
eners and flow promoting agents may often be sprayed
onto or otherwise mixed with the base beads or spray
dried detergent composition, with any nonionic deter-
15 gent and/or independently, so that they will not be ad-
versely affected by the elevated temperatures of the
spray drying operation and also so that their presence
in the spray dried beads does not inhibit absorption
of nonionic detergent, when such is to be post-sprayed
20 onto the beads. However, for stable and normally solid
adjuvants, mixing with the starting slurry in the crut-
cher is also feasible. Thus, it is contemplated that
pigments and fluorescent brighteners, when employed,
will normally be present in the crutcher mix from which
25 the present base beads are sprayed. The preferred color-

ing agent is ultramarine blue but other stable pig-
ments and dyes may be used with it or in replacement
of it. Because the spray dried base beads of this
invention sometimes may be off-color, usually due to
5 employment of naturally occurring minerals, the hue
from such coloring agent may be adversely affected.
It has been found that incorporating a small proportion
of titanium dioxide in the crutcher mix helps to retain
the desired hue of the coloring agent and the presence
10 of the titanium dioxide does not appear to have any ad-
verse affect on the appearance of laundry washed with
detergent compositions made from base beads containing
it.

Among the fluorescent brighteners the most pre-
15 ferred is Tinopal 5BM, especially in extra concentrated
form. 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 diaminostilbene disulfonic acid,
20 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 deter-
gent art and will most often be used when bleaching com-
ponents are not present in the final product. When it
25 is desired for the detergent composition to include a

bleach, such as sodium perborate or other oxidizing
bleach, bleach stable brighteners will usually be
incorporated in the crutcher mix. Among these there
may be mentioned the benzidine sulfone disulfonic
5 acids, naphthotriazol stilbene sulfonic acids and
benzimidazolyl derivatives. Polyamide brighteners,
which also may be present, include aminocoumarin or
diphenyl pyrazoline derivatives, and polyester bright-
eners, which can also be used, include naphthotriazo-
10 lyl stilbenes. Such brighteners are normally used as
their soluble salts but they may be charged as the cor-
responding acids. The cotton brighteners will usually
comprise major proportions of the brightener systems
employed.

15 Enzyme preparations, which normally are post-
added to the base beads because they are heat sensitive,
may be any of a variety of commercially available pro-
ducts, included among which are Alcalase, manufactured by
Novo Industri, A/S, and Maxatase, both of which are al-
20 kaline proteases (subtilisin). Maxazyme 375 is some-
times preferred. Although the alkaline proteases are
most frequently employed, amylotic enzymes, such as al-
pha-amylase, may also be utilized. The mentioned com-
positions usually contain active enzymes in combination
25 with an inert powdered vehicle, such as sodium or cal-

cium sulfate, and the proportion of active enzyme may vary widely, usually being from 2 to 80% of the commercial preparation. In this specification proportions referred to are of the enzyme preparations, not the active part thereof only. Perfumes employed, which are usually heat sensitive and may contain volatiles, including a solvent, such as alcohol, are normally of synthetic perfumery materials, sometimes mixed with natural components, and generally will include alcohols, aldehyde terpenes, fixatives and other normal perfume components. Flow promoting agents, such as special clays, which are sometimes added 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 and the absence or very limited presence of silicate. However, they may be added if desired, to further increase flowability. While it has been found that detergent compositions made from the present base beads do not require the presence of any anti-corrosion additive to replace the omitted silicate, it is within the invention to utilize suitable such materials and it will be preferred to employ those which are stable under crutching and spray drying conditions and which do not adversely affect such operations. Such anti-corrosion additives or antioxi-

dants may be organic or inorganic, with inorganic materials normally being preferred, and they will preferably be chosen for suitably for preventing corrosion of aluminum parts of washing machines. If
5 it is desired to continue to utilize a silicate for such purpose or to employ a silicate for its magnesium ion hardness treatment effect, a powdered silicate will normally be preferably, such as hydrous sodium silicate, which is commercially available under
10 the name Britesil[®], manufactured by Philadelphia Quartz Co. ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$), and such will preferably be post-added. However, other normally solid soluble silicates, preferably of alkali metals, may also be
15 post-added to the beads of this invention, preferably after any absorption of nonionic detergent that is to be effected.

When it is desired for the product made to possess textile softening characteristics, softening materials, preferably in dry powder form, may also be post-
20 added to the base beads in suitable manner. This class of materials is well known and most generally such softeners are cationic compounds, particularly quaternary ammonium compounds, such as quaternary ammonium halides. Especially preferred are the higher alkyl-, alkylaryl-
25 and arylalkyl-lower alkyl quaternary ammonium chlorides

and bromides, such as distearyl dimethyl ammonium chloride. Of commercial softening materials that which is most preferred is sold under the trade name Arosurf TA-100, manufactured by Sherex Chemical Company, Inc.

5 Such compounds possess anti-static and antibacterial properties too but if desired, other antibacterial adjuvants may also be employed, preferably also incorporated in the product by post-addition.

Of course, water is present in the crutcher to serve as the medium for dispersing the various other beads components, and some water, in both free and hydrate form, is in the product. During drying of the beads the initial moisture content thereof, which will be about 25 to 60% may be lowered to about 5 to 15%,

10 with such moisture content being sufficient so that the bentonite in the dried beads contains at least 2% and preferably at least 4% of moisture. It is preferred to employ deionized water, so that the hardness ion contents thereof may be very low and so that metallic ions that

15 can promote decomposition of any organic materials which may be present in the crutcher mix, base beads and detergent are minimized, but city or tap water may usually be employed 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.

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and most preferably it will be less than 50 p.p.m.

The proportions of the various components in the base beads and in the spray dried detergent composition beads will be such as to result in their being free flowing and, for the base beads, sufficiently absorptive of a nonionic detergent applied thereto in liquid state so that the detergent compositions will be satisfactorily free-flowing. Also, of course, the detergent compositions will be effective cleaning agents, with the builders present acting to assist the organic detergent in its deterative effect in aqueous solutions of the compositions, and it is important that the resulting products be such that they do not cause objectionable depositions of zeolite particles (or zeolite-silicate aggregates) on washed materials. The zeolite particles and the bentonite particles, although insoluble, will not objectionably discolor or lighten colored laundry as charged, because of their small particle sizes, but such discoloration can occur when zeolite aggregates are formed which are sufficiently large so as to be held to fabrics and also to be readily noticeable to the eye, especially when substantial proportions thereof are not removed from the laundered materials by being exhausted with the drying air during automatic drying. It is also desirable for the base beads and detergent composition beads made to be of appropriate bulk density and

color.

5 It has been found that satisfactory beads to accomplish the aforementioned purposes comprise by weight from 5 to 60% of water softening aluminosilicate (zeolite), 2 to 40% of bentonite (of the desired moisture content) and 5 to 60% of water soluble builder or mixture of such builders. From 0 to 30% of water soluble synthetic organic detergent and/or from 0 to 5% of water soluble silicate may also be present but often are preferably omitted. Preferably, the spray dried beads will contain from 3 to 15% of moisture, more preferably from 5 to 12% thereof and usually from 7 to 10% thereof, including any water of hydration present. Such water of hydration may be present in the zeolite, NTA, phosphate, carbonate, bicarbonate and magnesium sulfate, when such are in the formula, in addition to that between the plates of the bentonite. The recited moisture content includes even strongly held water of hydration, such as that still retained by the zeolite even after several hours of distillation of a toluene dispersion. In some instances, as when the concentration of zeolite in the product is high, so that up to about 12 to 15% of moisture could be present in the zeolite as water of hydration, the moisture content in the spray dried beads may be as high as 20% and occasionally, may

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go up to about 25%. Normally, however, for good flow-ability of the product and to minimize tackiness and lumping, such upper limit will be about 15%, especially when the final detergent composition contains an appreciable proportion of nonionic detergent. The percentage of zeolite given includes the water of hydration therein. It is possible to make useful spray dried of moisture contents less than 3% providing that the bentonite has sufficient water associated with it, for the reasons previously given, but due to the strong attraction for moisture of the zeolite and due to the actions of the other hydratable materials that may be present it has usually been found that a minimum of 3% of moisture is needed to avoid loss of the desired internal moisture of the bentonite, which appears to "lubricate" the plates and facilitate their separation when a product containing them is dispersed in water. Also, when anhydrous products are made, even when sufficient moisture is retained in the bentonite, they are liable to be physically unstable, powdering more readily and being subject to attrition and disintegration.

The bulk density of the spray dried beads may be within the range of 0.2 to 0.9 g./cc. Bulk densities in the lower part of this range are more readily obtainable when there is no silicate in the crutcher mix being

spray dried and when little or no nonionic detergent is absorbed by the beads. The higher bulk densities result when nonionic detergent is applied to porous beads and when some silicate is present in the beads.

5 Such lighter products have bulk densities in the 0.2 to 0.5 g./cc. range, often 0.3 to 0.4 g./cc., and the heavier particles are of bulk densities in the 0.6 to 0.9 g./cc. range, usually 0.6 to 0.8 g./cc. The bead particle sizes will usually be in the range of No's

10 10 to 100 (through No. 10 and on No. 100), U.S. Sieve Series, more preferably 10 to 60, U.S. Sieve Series. In preferred formulations the proportion of bentonite to zeolite is in the range of 1:4 to 1:1, the proportion of water soluble builder to zeolite is within the range

15 of 1:2 to 3:1 and the proportion of bentonite to water soluble builder is within the range of 1:10 to 1:1. More preferably, such ranges of ratios are 1:3 to 2:3 to 2:1, 1:6 to 1:2, respectively. Percentagewise, the compositions preferably comprise from 10 to 40% of a partially

20 hydrated sodium zeolite, preferably containing from 15 to 25% by weight thereof of water of hydration and with an exchange capacity for calcium ion in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, 2 to 35% of bentonite

25 which is of a type which has a swelling capacity in the

range of 7 to 15 ml./g. and is of a viscosity in the range of 8 to 30 cp. at 6% concentration of water, 10 to 50% of water soluble alkali metal builder salt or mixture thereof, 0 to 25% of water soluble synthetic anionic organic detergent and 0 to 3% of water soluble silicate, which silicate, when present, is an alkali metal silicate of alkali metal oxide : silicon dioxide ratio in the range pfl:1.6 to 1:3 more preferably 1:2 to 1:2.8. More preferred bead formulas include 15 to 35% of zeolite A, 5 to 20% of beneficiated Wyoming bentonite, 20 to 50% of water soluble sodium builder salt or mixture thereof, 0 to 20% of water soluble synthetic anionic organic detergent and 0% of sodium silicate.

Although carbonate and bicarbonate builders are useful in making base beads within this invention, especially those onto which nonionic detergent is to be sprayed, polyphosphate and/or nitrilotriacetate builder are often preferably for the spray dried beads, whether such include anionic detergent or not, and whether or not intended to have nonionic detergent applied to them. Preferred formulas of base beads based on NTA as the sole or main soluble builder include from 15 to 35 or 40% of hydrated zeolite, 5 or 10 to 20% of bentonite, and 20 to 50 or 60% of NTA. When a phosphate, such as sodium tri-

polyphosphate, is to be the principal or basic water soluble builder, the same proportions of zeolite and bentonite may be employed, but usually more phosphate can be present (than NTA). Preferably, for such base beads onto which nonionic detergent is to be sprayed or for comparable compositions based on carbonate or a mixture of bicarbonate and carbonate (with the ratio of carbonate:bicarbonate in the spray dried base beads being within the range of about 1 to 3), there will be no water soluble synthetic organic detergent and little or no water soluble silicate present. When bicarbonate and carbonate together are employed in such formulations they will usually total from 20 to 40% of the base beads and when carbonate alone is employed it will normally be 10 to 30% thereof.

When an anionic detergent or other suitable organic detergent is included in the crutcher so as to produce a spray dried detergent product preferred proportions thereof will be 3 or 5 to 30%, more preferably 5 to 25%, and most preferably 10 to 25%, e.g., 10%, 15%, of such product, and the detergent will preferably be selected from the group consisting of sodium linear alkyl benzene sulfonate wherein the alkyl is of 10 to 18 carbon atoms, sodium fatty alcohol sulfate wherein the alcohol is from 10 to 18 carbon atoms and sodium fatty al-

cohol ethoxylate sulfate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mole, and mixture thereof. At present, the most preferred of the detergents is sodium linear tridecyl benzene sulfonate, and alkyls are preferably of 12 to 16 carbon atoms.

When a nonionic detergent is absorbed into the spray dried base beads (and sometimes a small proportion may be absorbed into the spray dried detergent beads) the proportion thereof will usually be within the range of 5 or 8 to 30%, preferably 10 to 25%, e.g., 15%, 20%. In such case the preferred nonionic detergent is a condensation product of 6 to 12 mols of ethylene oxide and one mol of a higher fatty alcohol of 12 to 16 carbon atoms.

When polyacrylate is present in any of the detergent compositions or base beads it will normally be from 0.05 to 1% thereof and its molecular weight is preferably within the range of 1,000 to 5,000.

Because the presence of anionic detergent in the spray dried detergent beads may inhibit the production of a bead structure which will be absorptive of a desired proportion of nonionic detergent it may be prepared to produce spray dried detergent beads of a type within this invention and mix them with invented base

beads onto which nonionic detergent has been sprayed, so that a higher proportion of nonionic detergent may be present in the finished product. To do this varying ranges of proportions may be employed, e.g., 1:10 to 10:1, 1:5 to 5:1 and 1:2 to 2:1 of the mentioned components, depending on the characteristics wanted in the final product. It will be desirable for the bulk densities of the beads before mixing to be approximately the same, preferably within 0.1 g./cc. of each other and the particle sizes should be approximately the same, normally being within the No. 10 to 100, U.S. Sieve Series range, to prevent sifting and separation of the final mix .

Proportions of adjuvants and processing aids in the base beads and spray dried detergent 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 employed, will normally be from 0.5 to 2% of magnesium sulfate, preferably 1 to 1.5% thereof, and 0.1 to 0.5% of sodium citrate, preferably 0.1 to 0.3% thereof. With respect to coloring, pigmenting and fluorescent brightening agents, when respect, the proportions will normally be from 0.05 to 0.6% of coloring pigment, such as ultramarine blue, preferably 0.2 to 0.4%.

and 0.1 to 4% of fluorescent brightener, preferably
1 to 3% thereof. The proportion of titanium dioxide
(a whitening pigment) will normally be from 1 to 3%,
preferably 1.5 to 2.5. If a coloring dye or dyes
5 are used instead of a coloring pigment, proportions
will usually be 1 to 50%, especially 5 to 20% of
those of the coloring pigments.

For preferred spray dried beads within this in-
vention, which may contain NTA or polyphosphate build-
ers with or without synthetic organic detergent, or
10 may contain such detergent with any of a previously
given list of preferred water soluble builder salts, the
bulk density is in the range of 0.2 to 0.8 g./cc., the
aluminosilicate is hydrated zeolite A, the bentonite in-
cludes at least 3% moisture on an anhydrous bentonite ba-
15 sis, the water soluble silicate, if present, is sodium
silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:2 to 1:2.8,
and the moisture content of the beads is from 3 to 12%
thereof. When the beads contain NTA or other sodium salt
of nitrilotriacetic acid, with or without synthetic orga-
20 nic detergent, proportion of bentonite: zeolite is in the
range of 1:6 to 1:2, that of NTA; zeolite is in the range
of 1:2 to 2:1, and that of bentonite;NTA is in the range
of 1:6 to 1:2, and the percentages of hydrated zeolite,
25 bentonite, sodium nitrilotriacetate, and silicate are res-

pectively, within the ranges of 10 to 40%, 2 to 25%,
10 to 40%, and 0 to 5%.

5 When the preferred NTA-containing beads also
contain a synthetic anionic organic detergent, with the
aforementioned zeolite A, bentonite and moisture, and
with or without soluble silicate, they preferably com-
prise 5 to 30% of synthetic anionic organic detergent,
which will be sodium linear alkyl benzene sulfonate where-
in the alkyl is of 10 to 18 carbon atoms, sodium fatty al-
10cohol sulfate wherein the alcohol is of 10 to 18 carbon
atoms, or sodium fatty alcohol ethoxylate sulfate wherein
the fatty alcohol is of 10 to 18 carbon atoms and which
contain from 3 to 30 ethylene oxide groups per mol, or a
mixture comprising two or more thereof, the water soluble
15 builder is a sodium salt of nitrilotriacetic acid (NTA),
the proportion of bentonite; zeolite is in the range of
1:6 to 1:1, that of NTA: zeolite is in the range of 1:3
to 3:1, that of bentonite: NTA is in the range of 1:10 to
1:1, and that of synthetic anionic organic detergent: zeo-
20lite is in the range of 1:1 to 1:4, and the percentages
of hydrated zeolite, bentonite, sodium nitrilotriacetate,
synthetic anionic organic detergent, and silicate are res-
pectively, within the ranges of 10 to 40%, 2 to 25%, 10 to
40%, 10 to 25% (more preferred range), and 0 to 5%.

25 For phosphate-containing beads, with or without the

synthetic detergent the materials and ratios are
the same as for the corresponding NTA-containing
beads, with pentasodium triphosphate or tetra-
sodium pyrophosphate or a mixture thereof substitu-
5 ted for NTA, but the percentages are within the
ranges of 15 to 35%, 5 to 20%, 15 to 40% and 0 to 5%,
respectively, instead. Similarly, for the phosphate
containing beads with anionic detergent also present,
the materials and ratios are the same as for the cor-
10 responding NTA-containing beads and the percentage
ranges are the same except for that for total poly-
phosphate, which is 10 to 50%.

The ranges of proportions of the various base
bead components in the final detergent composition,
15 when nonionic detergent (possibly with other materials)
is post-added may readily be calculated from those gi-
ven for the base beads, diminished by proportions of
the detergent and other materials that are post-added
to the beads. Conversely, the bead component propor-
20 tions (and from them the crutcher mix formula) may be
calculated back from the final product formulation. Thus
for example, calculating the final product formula ranges
from the bead ranges, if the final detergent composition
had only nonionic detergent added to it so that the final
25 product contains 20% of nonionic detergent, from the va-

rious ranges given for components in the base beads
ranges of proportions thereof in the final deter-
gent composition product may be calculated by multi-
plying by 0.8, which is $(100-20)/100$. Similarly,
5 when the proportion of nonionic detergent (in formu-
las wherein it is the only additive to the beads) may
range from 8 to 25% of the detergent composition, the
multipliers will be from 0.92 to 0.75. The final per-
centage of nonionic detergent in the product will be
10 in the 8 to 30% range, preferably being 10 to 25% and
more preferably being 15 to 22%, e.g., about 20%, but
in some situations, for certain types of products,
proportions in the 8 to 13% range may be preferred. Nor-
mally, the percentage of perfume in the final product
15 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%,
preferably 1 to 2%, and if a hydrous sodium silicate is
to be post-added the proportions thereof will usually
be no less than 1% and is preferably limited to about 5%,
20 although in some cases as much as 10% has been used. When
a softening compound is present in the final product the
proportion thereof will normally be in the range of 3 to
12%, preferably 5 to 10%.

25 The base beads and the spray dried detergent beads
of the invention are spray dried from an aqueous crutcher

5 mix which normally will contain from about 40 to
about 70 or 75% 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 is
preferably made by sequentially adding various com-
ponents thereof pumpable and non-setting slurry for
spray drying. The order of addition of the materials
may be varied, depending on the circumstances, but it
10 is highly desirable to add the silicate solution (if
any) last, and if not last, at least after the addi-
tion of any gel- or "freeze"-preventing combination
of materials or processing aids, such as citric acid
and magnesium sulfate. Normally it is preferable for
15 all or almost all of the water to be added to the crut-
cher first, preferably at about the processing tempera-
ture, after which the processing aids (if present) and
other minor components, including pigment, and fluores-
cent brightener and polyacrylate, if present, are added,
20 followed by the zeolite, water soluble builder, anionic
detergent (if present), bentonite and silicate (if pre-
sent). Usually during such additions each component will
be mixed in thoroughly before addition of the next com-
ponent but methods of addition may be varied, depending
25 on the circumstances, so as to allow-co-additions when

such are feasible. Sometimes component additions may be in two or more parts and sometimes different components may be pre-mixed before addition, to 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 zeolite or soluble builder, after which the speed may be increased to medium and then to high, at which it will preferably be before, during and after addition of any 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 80% range, preferably from 30 to 75 or 80%, and more preferably 40 to 70°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 and can sometimes promote setting of the mix. An advantage of having processing aiding materials present in the mix (especially if any soluble silicate is present) is that they ensure that at higher and lower temperatures non-gelling slurries will result. Temperatures higher than 80°C. (and sometimes those higher

than 70°C.) will usually be avoided because of the possibility of decomposition of one or more of the crutcher mix components, e.g., sodium bicarbonate. Also, in some cases lower crutcher temperatures increase the upper limits of crutcher solids contents, probably due to insolubilizing of normally gelling or setting components.

Crutcher mixing times to obtain good slurries can vary widely, from as little as five minutes in small crutchers and for slurries of higher moisture contents, to as much as four hours, in some cases. The mixing times needed to bring all the crutcher mix components substantially homogeneously together in one medium may be as little as ten minutes but in some cases can take up to an hour, although 30 minutes is a preferable upper limit. Counting any such initial admixing times, normally crutching periods will be from 15 minutes to two hours, e.g., 20 minutes to one hour, but the crutcher mix should 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 the mix, and preferably will be mobile for as long as 10 to 30 hours before pump-out to the spray tower, to allow 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 form, uniformly distributed therein, is transferred in usual manner to a spray drying tower which is normally located near the crutcher. The slurry is 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, usually the combustion products of fuel oil or natural gas, in which the droplets are dried to desired bead form. During the drying, part of the bicarbonate (if present) may be converted to carbonate, with the release of carbon dioxide, which, in conjunction with any of the polyacrylate present in the mix being spray dried, improves 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, bentonite and polyphosphate (when present) components of the base beads made also appear to favor absorption of liquid and the production of a strong bead, and the polyacrylate improves bead characteristics and promotes faster drying, thereby increasing tower

throughout.

After drying, the product is screened to desired size, e.g., 10 to 60 or 100, U.S. Sieve Series, and is ready for application of nonionic detergent spray thereto, if it is a base bead formula, with the beads being either in warm or cooled (to room temperature) condition. However, the nonionic detergent will usually will usually be at an elevated temperatures, such as 30 to 60°C., e.g., 50°C., to ensure that it will be liquid; yet, upon cooling to room temperature, it will desirably be solid, often resembling a waxy solid. Even if at room temperature the nonionic detergent is somewhat tacky, this characteristic does not make the final composition poorly flowing because the detergent penetrates to below (or within) the bead surface. The nonionic detergent, applied to moving or tumbling beads in known manner, as a spray or as droplets, is preferably a condensation product of ethylene oxide and higher fatty alcohol, such as was previously described, but other nonionics may also be operative. The enzyme preparation (herein referred to as enzyme, although it is recognized that it includes a carrier material, too), hydrous silicates and any other powdered adjuvants may be dusted onto the detergent particles, and perfume and any other liquids to be post-added may be sprayed on at a suitable

point before or after addition(s) of the powder(s).

5 The spray dried detergent, the spray dried
base beads and the detergent compositions made from
them include little or no silicate from the crutcher
mix, although some silicate in solid form may be post-
10 added. The post-added powdered silicate, if employed,
does not seem to react with the zeolite as much, so
zeolite-silicate agglomerations that tend to deposit
on laundered articles are reduced, compared to such de-
15 posits from products wherein silicate was added in the
crutcher. Although, without the bentonite being pre-
sent, silicates would normally be used for its bead con-
trolling and anti-corrosion effects, the present deter-
gent compositions produce acceptable beads and have not
20 been found to cause the corrosion of aluminum articles.
Furthermore, the bentonite does not adversely affect the
stability of the product and in fact, appears to help to
hold the beads together, making them resistant to crushing
and powdering during shipment and use. The presence of
25 the bentonite significantly improves the properties of the
final detergent composition, resulting in higher calcium
ion binding rates and in less zeolite being deposited on
laundered fabrics. When the low molecular weight poly-
acrylate is present the base 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 serves as a binder, it might be expected to create deposition and gelation problems of its own. Therefore, the lowered deposition characteristics, absence of gelation,
5 and ready product dispersion are surprising, and they are important results of the present invention. Also considered to be important results of the presence of the small proportion of polyacrylate in the spray dried beads is the improved spray drying of the present base beads
10 and detergent compositions, and the improved sorption of liquid nonionic detergent by the base beads.

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
15 examples and throughout the specification. 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
20 leave the zeolite and does not become part of the aqueous solvent medium in the present crutching operations. Also, part of the water present in the base beads and the detergent compositions is present as water of hydration of the zeolite. Similarly, the moisture associated with the bentonite may also be considered not to be free moisture but
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because of the lesser percentage present this distinction can often be neglected, as a practical matter.

EXAMPLE 1(Comparative)

5 A 100 parts batch of crutcher mix for spray drying base beads considered as satisfactory for subsequent conversion to a detergent composition by addition of synthetic nonionic organic detergent thereto is made by adding to the crutcher 47 parts of deionized water at a
10 temperature of about 27°C. (80°F.), and then sequentially, and initially with low speed crutcher mixing, admixing with it 1.04 parts of Tinopal 5BM Extra Conc. (CIBA-Geigy), 0.13 part of ultramarine blue powder, 0.07 part of sodium polyacrylate (Alcosperse 107D), 21.11 parts of Linde hydrated zeolite 4A (20% water of crystallization), 6.25
15 parts of Mineral Colloid No. 1 (bentonite), 15.75 parts of sodium bicarbonate (industrial grade), 7.74 parts of sodium carbonate (natural soda wash) and 0.91 part of titanium dioxide (anatase). During mixing of the various components the mixer speed is increased to medium and ultimately to high and after addition of all the constituents, which takes approximately fifteen minutes, mixing is continued for about an hour (in some cases as four hours of mixing may occur), during which time some of the water
20 present, e.g., about two to six parts, may be lost by
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evaporation, and 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 of bicarbonate and carbonate in the crutcher formulation may be varied, depending on the spray tower operating characteristics.

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 21 kg./sq. cm. into the top of a countercurrent spray tower wherein the initial temperature is about 430°C. and the final temperature is about 105°C. The essentially inorganic base beads resulting are of a bulk density of about 0.6 to 0.7 g./cc., an initial adhesion less than 10%, a particle size range substantially between 10 and 60 mesh, U.S. Sieve series (they are screened to such range), and a fines characteristic (through U.S. Sieve No. 50) of about 15%. The moisture content of the beads is in the range of 1 to 10%, normally being closer to 10%, e.g., 8 to 10%. The base beads are found to be free flowing (80% flow rate), non-tacky, satisfactorily porous, yet firm on the surfaces thereof. They 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 normally waxy nonionic detergent. Neodol 23-6.5 is used but Neodol 23-7 or Neodol 25-7 (and sometimes Neodol 45-11) may be substituted. The nonionic detergent is in heated liquid state (at a temperature of about 45°C.) The quantity sprayed is such as to result in a final product containing about 20% of nonionic detergent. Proteolytic enzyme (Alcalase 1.7T or Maxazyme 375) is applied in powdered form to result in about a 1.5% concentration in the product, and perfume is sprayed onto the product to produce a 0.25% concentration therein. The resulting detergent compositions are of a bulk density of about 0.7 to 0.8 g./ml. and contain about 32.45% of zeolite (hydrated), 19.7% of the nonionic detergent, 18.5% of sodium carbonate (some of which was produced by decomposition of sodium bicarbonate), 13.5% of sodium bicarbonate, 1.3% of free water, 1.4% of enzyme, 1.6% of fluorescent brightener, 0.25% of perfume, 0.2% of ultramarine blue, 9.6% of bentonite, 0.1% of sodium polyacrylate and 1.4% of titanium dioxide.

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 advanced.

tageous and attractive because it is non-dusting and extremely freely flowing, which allows it to be packaged in narrownecked glass and plastic bottles, from which it flows readily for dispensing. The detergent compositions produced, containing bentonite, as described, are of improved calcium ion binding rates but more importantly, they leave less zeolite residue on laundry washed with them (in an automatic washing machine at usual concentrations for such products and at normal wash temperatures), especially when such laundry is line dried, than do similar compositions containing less bentonite and with sodium silicate in the spray dried base beads. 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.

The base beads and detergents composition made are acceptable standards against which the other described beads and detergent compositions of the following examples may be measured, and to which they compare favorably. Also, the manufacturing methods are essentially the same and are considered to be satisfactory.

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 some times holdups of such lengths of time 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 gelling or solidifying, which is attributed, at least in part, to the content of bentonite and the absence of silicate. This action of the bentonite is unexpected because it also has a thickening effect on the crutcher mix, but although the mix may thicken appreciably it remains pumpable. 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 mixes that result in the desired beads and detergent compositions will be obtainable. The crutcher mix solids contents may be varied over

the range recited, e.g., to 45% and 65%, and good mixing and spray drying result. Other orders of addition to the crutcher of components may be employed but normally it will be desired to add any silicate last or near the end, and it is preferred that the bentonite also be added late in the process, preferably just before the silicate. Instead of using Zeolite 4A, Ceolites X and Y may be substituted, as may be other types of Zeolite A. While it is preferred to employ the approximately 80% hydrated Zeolite 4A (about 20% moisture content) 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 7%, 13% and 19% in the base bead, for example, still results in useful products, but those containing the larger proportions of bentonite will usually be more effective in helping to prevent zeolite deposition on laundry. In some instances it may be desirable to utilize even higher percentages of bentonite, within the ranges set forth in this specification, taking care that the other components of the base bead will be such that the beads will be free flowing and effective detergents. The proportion of bentonite suitable to be 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 that could be incorporated in place of an increased amount of bentonite.

The improvement noted in the detergent composition of this example depositing less residue on washed laundry is verified by testing the described product against a control product of essentially the same formula, with no bentonite present and containing about 8% of sodium silicate in the final product. In this evaluation a Whirlpool Suds Saver model washing machine is employed, with the washing periods being eight minutes at a gentle wash cycle. The detergent composition concentration is 0.06%, the wash water is of mixed calcium and magnesium hardness with a total of 200 p.p.m. hardness, as calcium carbonate, and the water temperature is 24°C. The items washed are: 100% cotton; 100% polyester; 85% acetate and 15% nylon; and 65% polyester and 35% cotton. The wash is observed wet and after line drying (line drying usually results in more visible residue than does automatic dryer drying). No residue is observed in either such case. When the control formula detergent composition is tested, moderate residue is observed

on all washed specimens.

The results of the practical residue test described above are verified by weighing residue deposited on a denim test material. In such test, the detergent composition of this invention is filtered through a sample of denim material, with the detergent being in solution -suspension at 0.12% concentration in 200 p.p.m. (as CaCO_3) hardness water at 24°C ., and the weight of residue on the cloth is noted, and compared. By such test percentage of residue, compared to the control, is about 75%, which is considered to represent a significant difference in appearance of washed products.

The adhesion test, previously referred to, which measures tackiness of detergent product, is one in which 10 grams of base beads (or detergent composition, in some cases) are placed evenly between two watch glasses, both of which are 23 cm. in diameter, with a weight of 500 grams on top of the upper watch glass (both watch glasses being concave side up). After standing there five minutes, the weight and top watch glass are removed and the bottom watch glass is inverted, after which the product remaining stuck to such watch glass is weighed. The percentage adhesion is the number of grams of product remaining on such watch glass multiplied by 10.

The flow index is that resulting from a flow test

wherein the volumetric flow rates of base beads (and in some cases final product) and standardized Ottawa sand (-20 +60, U.S. Sieve Series) are compared by measuring the times required for complete emptying of a 1.9 liter Mason jar through a 2.2 cm. diameter circular hole in a nozzle attached to the cap thereof. The flow index % is the time for the sand flow divided by the time for the test product flow, times 100.

EXAMPLES 2

Base beads like those of Example 1 but with NTA included therein in place of some of the carbonate and bicarbonate are made by essentially the same method described in that example. The formula is changed only by replacing 5 parts of the zeolite, 12 parts of the sodium bicarbonate and 3 parts of the sodium carbonate in the crutcher with 20 parts of NTA, as the trisodium salt monohydrate. The NTA is added after the sodium carbonate during the mixing operation. The base beads obtained are not as crisp as those of Example 1 but are sufficiently satisfactorily free flowing. Instead of the final detergent composition containing 19.7% of the nonionic detergent, it is sufficient for it to hold 12%, with the final percentages of the other components being increased accordingly. The resulting product is a satisfactory heavy duty particulate detergent.

In variations of this formula, 2.5% of hydrous sodium silicate is post-added to the product for its anti-corrosion properties and for its utility in tying up magnesium ions in the wash water. Providing that the silicate is of about the same particle size and density it does not shift or segregate from the other detergent bead components during shipping and storage, and the resulting product meets specifications for a zeolite-silicate aggregate may be noted on washed materials.

In another alternative formula, 3% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.4 is included in the final product by addition of an aqueous solution thereof in the crutcher, together with 1.5% of magnesium sulfate and 0.4% of citric acid to prevent gelation or setting in the crutcher. The finished product is a good heavy duty detergent but does deposit more zeolite-silicate aggregate on washed materials that are line dried than does a comparable formula to which the hydrous sodium silicate is post-added.

EXAMPLE 3

The procedure of Example 2 is repeated but with pentasodium tripolyphosphate being substituted for the NTA. The products obtained are good detergents, of a bulk density of about 0.8g./cc. (as are those of Example 2) but such den-

sities may be varied by adjustment of spray tower conditions and formulas so as to be within the range of 0.7 to 0.9, and in some cases the densities may be lowered to 0.3. With the post-added silicate the densities may be slightly higher, especially for those in the lower portion of the range. The product is more free flowing than that of Example 2 but is about equivalent to it washing power.

In the above formula and those of the previous examples an additional proportion of bentonite may be added in the crutcher to make products containing 15% (or more) of the bentonite. Such products are even better in binding effects, dispersibility and other desirable properties attributable to the bentonite and are good detergent (and base bead) preparations. Also, the tripolyphosphate may be replaced, either in whole or in part, e.g., 1/2, by tetrasodium pyrophosphate, and similar good products result.

EXAMPLE 4

A final detergent product is made essentially by the method of Examples 1 and 2 containing 30 parts of the zeolite, 30 parts of NTA, 20 parts of the nonionic, 10 parts of bentonite, 5 parts of sodium carbonate, 5 parts of sodium carbonate, 5 parts of water and 1.3 parts

of enzyme. This product has a density of about 0.5 g./cc. and is a satisfactory detergent. However, to improve flowability of the product it is desirable for the nonionic detergent content to be decreased to 15% and preferably to 12%. To increase the bulk density to about 0.7, half of the bentonite may be replaced by sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4), added as the last component in the crutcher as a 47.5% aqueous solution, and 1.5 parts of magnesium sulfate and 0.4 parts of citric acid may be correspondingly added as anti-gelling agents earlier in the making of the crutcher mix. The resulting product is of about 0.7 g./cc. bulk density and can absorb about 20 parts of nonionic detergent without becoming tacky or of diminished flowability. While it deposits less zeolite-silicate agglomerate than formulations with conventional greater proportions of silicate present from crutcher additions the agglomerate can be detected on laundry washed with the product and line dried.

EXAMPLE 5

Instead of manufacturing base beads to which detergent is applied to form a detergent composition the composition may be spray dried directly from the crutcher with a suitable synthetic organic detergent being included in the crutcher mix. Using essentially the same proce-

dures as described in Example 1, a crutcher mix is made which is spray dried to detergent beads containing 16 parts of linear tridecyl benzene sulfonate, 20 parts of the zeolite, 12.5 parts of bentonite, 15 parts of NTA, 10 parts of sodium carbonate and conventional adjuvants (colorants fluorescent brightener). The bulk density of the spray dried product will be in the 0.3 to 0.8 range, normally being in the lower portion of such range and sometimes being as low as 0.2 g./cc. In the manufacturing process the organic detergent will normally be added after the water. Drying will usually be to a moisture content of about 8 to 12%. The resulting product preferably has about 3 parts of hydrous sodium silicate post added, together with other normal adjuvants, such as enzyme and perfume. It is a satisfactory heavy duty detergent which does not deposit objectionable amounts of zeolite or zeolite-silicate aggregate on washed fabrics. Due to the presence of the bentonite the detergent appears to disperse very quickly when added to the wash water and it is considered that at least in part this quick dispersibility, together with the presence of the bentonite, tends to inhibit zeolite deposition.

EXAMPLE 6

The procedure of Example 5 is followed but the NTA is replaced by an equal weight of soda ash. Such product is also a satisfactory heavy duty detergent.

EXAMPLES 7

The procedure of Example 5 is followed but pentasodium tripolyphosphate is included in place of NTA. The product made is especially free flowing and is a good heavy duty synthetic organic detergent composition. Although when silicate is to be present it is preferred that it be post-added as a hydrous sodium silicate, up to 5 parts of silicate may be added in the crutcher, together with the appropriate proportions of magnesium sulfate and citric acid, as described in previous examples, and useful detergent compositions will result, although some zeolite-silicate deposition will occur.

In addition to the conventional materials which may be post-added, there may be added to the product of this example (and to the products of other examples), softening proportions of a cationic material, e.g., 8% of dimethyl distearyl ammonium chloride, an amphoteric detergent, e.g., 5% of Miranol C₂M (1-carboxymethyl-1-

carboxyethoxyethyl-2-coco-imidazolinium betaine), or
a bleach, e.g., 15% of sodium perborate (preferably
activated). Of course, the additions of such mate-
5 rials will diminish the proportions of the other com-
ponents in the final composition and thereby will change
the properties of the compositions somewhat, sometimes
requiring the use of more of the product in the wash wa-
ter to obtain the same cleaning effect.

10 In Examples 5-7 the linear tridecyl benzene sul-
fonate may be replaced with an equal weight of sodium
lauryl sulfate or sodium lauryl polyethoxy sulfate (3
to 10 EtO) or mixtures of such materials in equal parts
and the products obtained are also useful as detergent
15 compositions. Similarly, instead of the NTA, carbonate,
carbonate and bicarbonate, and polyphosphate, sodium ci-
trate and/or sodium glucomate may be substituted, at
least in part, e.g., 1/4, 1/2, and good detergents result.

EXAMPLE 8

20 The products of Example 1 and Example 7 (the pri-
mary products first described) are mixed in equal propor-
tion to obtain a final product with the characteristics
of both such constituent parts. Prior to mixing the ma-
terials to be mixed are both of approximately the same
25 bulk density, about 0.5 g./cc. and of about the same par-

ticle sizes, in the No's 10 to 60 range, U.S. Sieve Series, so as to prevent separation during shipping and storage. The mixed product is especially useful for the removal of both oil-based and clay-based on
5 laundry, and is free flowing, stable and attractive. In some cases one of the particulate starting materials may be dyed or pigmented and the other left natural in color to obtain special appearance effects. In addition to the particle sizes and densities being
10 about the same it is preferred that the moisture contents also be about the same, e.g. about 10%, so that there will be little migration of moisture between the different beads.

In the Example 7 materials used the anionic detergent may be changed from sodium alkylbenzene sulfonate to a sodium alpha-olefin sulfonate (14-15 carbon atoms in the olefins) or to a sodium paraffin sulfonate (12-15 carbon atoms in the paraffin) and the mixtures made
15 will also be useful detergents.

20 EXAMPLE 9

Following substantially the procedure described in Example 1 a crutcher mix is made from 36.9 parts of water, 1.2 parts of fluorescent brightener (Tinopal 5BM, extra concentrated) 0.1 part of ultramarine blue, 2.1.

parts of magnesium sulfate (heptahydrate), 0.3 part
of sodium citrate, 22.4 parts of zeolite 4A powder
(partially hydrated, to about 20% moisture content),
20 .9 parts of trisodium nitrilotriacetate monohydrate,
5 7.4 parts of a 47.5% solids solution of sodium sili-
cate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$), 3.7 parts of sodium bentonite
(formerly marketed as THIXO-JEL No. 2), 2.8 parts of
natural soda ash and 2.1 parts of a mineral type com-
pound, which may act to increase bead porosity, and as
10 a building agent . The crutcher mix is spray dried in
a manner like that previously described, with the moist-
ure loss in drying being about 45.2%.

Onto 78.4 parts of the spray dried base beads, of
particle sizes in the No. 10 to 100 range (screened),
15 are sprayed 20 parts of Neodol 23-6.5, after which the
beads are mixed with 1.3 parts of high activity proteo-
lytic enzyme, and 0.3 part of detergent perfume is spray-
ed onto them. The final product has a zeolite content of
25%, an NTA content of 30%, a sodium bentonite content of
20 5% and a water soluble sodium silicate solids content of
5%. The moisture content is 5% and the active deter-
sive ingredient (polyethoxylated higher fatty alcohol)
content is 20%. The bulk density is about 0.7 g./cc.
and the pH of its 1% solution is about 10.

25 The detergent composition made by this method is
a satisfactory heavy duty nonionic detergent but does de-

posit somewhat more zeolite-silicate aggregate on washed clothing that is line dried than does a corresponding composition made without any water soluble silicate solids. It is preferred that in such corresponding composition there is also present about 0.1 to 0.5% of low molecular weight sodium polyacrylate, of the type previously described herein. Both products wash laundry well and are especially effective in cold water washing, due at least in part to the bentonite contents thereof and the almost instantaneous dispersion that is observable when the detergent is added to wash water (which dispersion also diminishes time for any reaction between soluble silicate and zeolite to form objectionable aggregates).

WHAT IS CLAIMED IS:

5 1. Free flowing, spray dried beads, useful
as a detergent or for the manufacture of a parti-
culate built synthetic organic detergent composi-
tion, which detergents are of reduced particle de-
position characteristics due to the presence of ben-
tonite and a low content of water soluble silicate
or absence of such silicate in the spray dried beads
comprising by weight from 5 to 60% of water softening
10 zeolite which is a hydrated water softening zeolite
containing from 15 to 25% by weight of water of hydra-
tion and having an ion exchange capacity for calcium
ion which is in the range of 200 to 400 milligram equi-
valents of calcium carbonate hardness per gram of an-
15 hydrous zeolite. 2 to 40% of swelling bentonite, con-
taining sufficient moisture to facilitate dispersion of
the bentonite so as to inhibit deposition of zeolite on
the laundry being washed, 5 to 60% of water soluble
builder or a mixture of such builders 0 or 30% of water
20 soluble synthetic organic detergent and 0 to 5% of water
soluble silicate.

25 2. ^Beads according to claim wherein when water
soluble synthetic detergent is not present the water
soluble builder comprises polyphosphate, phosphate,
borate, nitrilotriacetate, gluconate or citrate or a
mixture of two or more thereof.

3. Beads according to claim 2, of a bulk density in the range of 0.2 to 0.9 g./cc. and particle sizes in the range of No. 10 to 100, U.S. Sieve Series wherein the water softening zeolite which is a hydrated water softening zeolite containing from 15 to 25% by weight of water of hydration and having an ion exchange capacity for calcium ion which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, is a hydrated water softening zeolite containing from 15 to 25% by weight thereof of 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 swelling bentonite is a swelling clay having a swelling capacity, in water, of 3 to 15 ml./g. and a viscosity of 3 to 30 centipoises at 6% concentration in water, and includes at least 2% of moisture on an anhydrous bentonite basis, a water soluble, builder is present which is polyphosphate, pyrosposphate, phosphate, borate, nitrilotriacetate, citrate, gluconate, carbonate or bicarbonate or a mixture of two or more thereof, and the water soluble silicate is an alkali metal (M) silicate of $M_2O:SiO_2$ ratio in the range of 1:1.6 to 1:3.

4. Beads according to claim 3 wherein the proportion of swelling bentonite to zeolite which is a hydrated

water softening zeolite containing from 15 to 25% by weight of water of hydration and having an ion exchange capacity for calcium ion which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite is a hydrated water softening zeolite containing from 15 to 25% by weight thereof of 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 swelling bentonite is a swelling clay having a swelling capacity, in water, of 3 to 15 ml./g. and a viscosity of 3 to 30 centipoises at 6% concentration in water, and includes at least 2% of moisture on an anhydrous bentonite basis, a water soluble builder is present which is polyphosphate, pyrophosphate, phosphate, borate, nitrilotriacetate, citrate, gluconate, carbonate or bicarbonate or a mixture of two or more thereof, and the water soluble silicate is an alkali metal (M) silicate of $M_2O:SiO_2$ ratio in the range of 1:1.6 to 1:3.

4. Beads according to claim 3 wherein the proportion of swelling bentonite to zeolite which is a hydrated water softening zeolite containing from 15 to 25% by weight of water of hydration and having an ion exchange capacity for calcium ion which is in the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite is in the range of 1:4 to 1:1, the pro-

portion of water soluble builder to zeolite is within the range of 1:2 to 3:1 and the proportion of swelling bentonite to water soluble is within the range of 1:10 to 1:1.

5 5. Beads according to claim 4 comprising from 10 to 40% of hydrated sodium zeolite, 2 to 35% of swelling bentonite, which bentonite is of a type which has a swelling capacity in the range of 7 to 15 ml/g. and is of a viscosity in the range of 8 to 30 cp at 6% concentration in water, 10 to 50% of water soluble alkali metal
10 builder salt or mixture thereof, 0 to 25% of water soluble synthetic anionic organic detergent and 0 to 3% of water soluble silicate.

15 6. Beads according to claim 5 comprising from 15 to 35% of zeolite A, 5 to 20% of beneficiated Wyoming bentonite, 20 to 50% of water soluble sodium builder salt or mixture thereof, 0 to 20% of water soluble synthetic anionic organic detergent and 0% of sodium silicate, and in which the proportion of bentonite; zeolite
20 is in the range of 1:3 to 2:3, that of water soluble builder; zeolite is within the range of 2:3 to 2:1 and that of bentonite; water soluble builder is within the range of 1:6 to 1:2.

25 7. Beads according to claim 2 wherein the water soluble builder is selected from the group consisting of

carbonate, bicarbonate, polyphosphate or nitrilotriacetate, or a mixture thereof, and the swelling bentonite includes at least 3% of moisture on an anhydrous swelling bentonite basis.

5 8. Beads according to claim 7 wherein the swelling bentonite includes at least 4% of moisture, the water soluble builder comprises a nitrilotriacetate and no water soluble synthetic organic detergent nor any water soluble silicate is present.

10 9. Beads according to claim 8 comprising from 15 to 40% of hydrated zeolite A containing 15 to 25% by weight thereof of water of hydration and having an exchange capacity for calcium ions which is the range of 200 to 400 milligram equivalents of calcium carbonate hardness per gram of anhydrous zeolite, 10 to 20%
15 of swelling bentonite which is a beneficiated Wyoming bentonite of swelling capacity in the range of 7 to 15 ml./g. and of a viscosity in the range of 3 to 30 cp at 6% concentration in water, and 20 to 60% of NTA.

20 10. Beads according to claim 7 wherein the swelling bentonite includes at least 4% of moisture, the water soluble builder comprises a polyphosphate and no water soluble synthetic organic detergent nor water soluble silicate is present.

25 11. Beads according to claim 10 wherein the anio-

nic detergent is sodium linear alkylbenzene sulfonate wherein the alkyl is of 10 to 18 carbon atoms, sodium fatty alcohol sulfate wherein the alcohol is of 10 to 18 carbon atoms, or sodium fatty alcohol ethoxylate sulfate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mol, or a mixture of two or more thereof, and the proportion of such anionic detergent(s) in the beads is from 5 to 25%.

10. 12. Beads according to claim 7 which comprises from 3 to 30 of water soluble synthetic anionic organic detergent.

15 13. Beads according to claim 12 wherein the anionic detergent is sodium linear alkylbenzene sulfonate wherein the alkyl is of 10 to 18 carbon atoms, sodium fatty alcohol sulfate wherein the alcohol is of 10 to 18 carbon atoms, or sodium fatty alcohol ethoxylate sulfate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mol, or a mixture of two or more thereof, and the proportion of such anionic detergent(s) in the beads is from 5 to 25%.

20 14. Beads according to claim 2 which comprise from 0.05 to 1% of polyacrylate of molecular weight in the range of 1,000 to 5,000.

15. Beads according to claim 3, of a bulk density in the range of 0.2 to 0.8 g./cc., wherein the zeolite is hydrated zeolite A, the swelling bentonite includes at least 3% moisture on an anhy-
5 drous swelling bentonite basis, the water soluble builder is a sodium salt of nitrilotriacetic acid, the water soluble silicate, if present, is sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:2 to 1:2.8, the moisture content of the beads is from 3 to 12% thereof, the
10 proportion of swelling bentonite: zeolite is in the range of 1:6 to 1:2, that NTA: zeolite is in the range of 1:2 to 2:1, and that of swelling bentonite: NTA is in the range of 1:6 to 1:2, and the percentages of hydrated zeolite swelling bentonite, sodium nitrilotriacetate, and
15 silicate are respectively, within the ranges of 10 to 40%, 2 to 25%, 10 to 40%, and 0 to 5%.

16. Beads according to claim 3, of a bulk density in the range of 0.2 to 0.8 g./cc. which comprises 5 to 30% of synthetic anionic organic detergent and in which the
20 zeolite is hydrated zeolite A, the swelling bentonite includes at least 3% moisture on an anhydrous swelling bentonite basis, the water soluble builder is a sodium salt of nitrilotriacetic acid, the synthetic anionic organic detergent is sodium linear alkyl benzene sulfonate where-
25 in the alkyl is of 10 to 18 carbon atoms, sodium fatty al-

cohol sulfate wherein the alcohol is of 10 to 18 carbon atoms, or sodium fatty alcohol ethoxylate sulfate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mol, or a mixture comprising two or more thereof, the water soluble silicate, is sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:2 to 1:2.8, the moisture content of the beads is from 3 to 12% thereof, the proportion of swelling bentonite: zeolite is in the range of 1:6 to 1:1, that of NTA : zeolite is in the range of 1:3 to 3:1, that of bentonite: NTA is in the range of 1:10 to 1:1, and that of synthetic anionic organic detergent : zeolite is in the range of 1:1 to 1:4 and the percentages of hydrated zeolite, swelling bentonite, sodium nitrilotriacetate, synthetic anionic organic detergent, and silicate are respectively, within the ranges of 10 to 40%, 2 to 25%, 10 to 40%, 10 to 25%, and 0 to 5%.

17. Beads according to claim 3, of a bulk density in the range of 0.2 to 0.8 g./cc., wherein the zeolite is hydrated zeolite A, the swelling bentonite includes at least 3% moisture on an anhydrous swelling bentonite basis, the water soluble builder is pentasodium tripolyphosphate or tetrasodium pyrophosphate or a mixture thereof, the water soluble silicate, is sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:2 to 1:2.8, the moisture content of

the beads is from 3 to 12% thereof, the proportion swelling bentonite: zeolite is in the range of 1:6 to 1:2, that of total polyphosphate: zeolite is in the range of 1:2 to 2:1, and that of bentonite: total polyphosphate is in the range of 1:6 to 1:2 and the percentages of hydrated zeolite swelling bentonite total polyphosphate, and silicate are respectively, within the ranges of 15 to 35%, 5 to 20%, 15 to 40% and 0 to 5%.

10 18. Beads according to claim 3, of a bulk density in the range of 0.2 to 0.8 g./cc. which comprise 5 to 30% of synthetic anionic organic detergent and in which the zeolite is hydrated zeolite A, swelling bentonite includes at least 3% moisture on an anhydrous
15 swelling bentonite basis, the water soluble builder is pentasodium tripolyphosphate or tetrasodium pyro phosphate or a mixture thereof, the synthetic anionic organic detergent is sodium linear alkyl benzene sulfonate wherein the alkyl is of 10 to 18 carbon atoms, sodium fatty alcohol sulfate wherein the alcohol is of 10
20 to 18 carbon atoms, or sodium fatty alcohol ethoxylate sulfate wherein the fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethylene oxide groups per mol, or a mixture comprising two or
25 more thereof, the water soluble silicate, if present,

is sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:2 to 1:2.8, the moisture content of the beads is from 3 to 12% thereof, the proportion of Swelling bentonite; zeolite is in the range of 1:6 to 1:1, that of total polyphosphate: zeolite is in the range of 1:3 to 3:1, that of swelling bentonite: total polyphosphate is in the range of 1:10 to 1:1, and that of synthetic anionic organic detergent :zeolite is in the range of 1:1 to 1:4 and the percentages of hydrated zeolite swelling bentonite, total polyphosphate, synthetic anionic organic detergent, and silicate are respectively, within the ranges of 10 to 40%, 2 to 25%, 10 to 50%, 10 to 25%, and 0 to 5%.

19. A detergent composition which comprises beads of claim 1 having absorbed in them a nonionic detergent so that the percentage of such nonionic detergent in the composition is within the range of 8 to 30%.

20. A detergent composition comprising a mixture of beads of claim 7 and of particle sizes in the range of No. 10 to 100 , U.S. Sieve Series, in a proportion, by weight, in the range of 1:10 to 10:1 and with the bulk densities of the beads before mixing thereof being within 0.1 g./cc. of each other and of the final composition bulk density, which is in the range of 0.2 to 0.9 g./cc.

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