

"FABRIC SOFTENING AND FLUFFING
DETERGENT COMPOSITION"

The present invention relates to detergent compositions and methods for the manufacture thereof. More particularly, it relates to detergent compositions which have fabric softening effects, very preferably accompanied by fabric fluffing effects, and to fabric softening and fluffing compositions which are useful additives for detergent compositions, making them capable of softening and fluffing laundry washed with such modified detergent compositions. The invention also relates to processes for the manufacture of such additives and of improved detergent compositions containing them.

Particulate laundry detergent compositions comprising organic detergent, builder(s) for such detergent and various suitable adjuvants have received wide acceptance and today are almost universally used for machine washing of laundry, fabrics and textiles. While such products satisfactorily clean the laundry when used in automatic washing machines, they often leave washed materials feeling less soft than is desirable. Accordingly, softening agents have been incorporated in detergent compositions to improve this characteristic of such products. Among such softening agents that have been found to be useful are clays of various types, preferably swellable clays,

and of these the bentonites have been successfully employed to give washed materials a softer feel. It has been theorized that this is accomplished by the very finely divided bentonite particles adhering to the washed goods and providing lubricious sliding plate-like structures on the fibres which lubricate them so that they slide past one another more readily, giving the impression of softness.

To obtain excellent softening effects of built detergent compositions comparatively large proportions of bentonite have been employed. While such proportions of bentonite are tolerable in many compositions, in others they may have negative effects. Thus, the bentonite, if used as in its natural clay form or if not whitened by processing may be of an off-colour and this could adversely affect the appearance of a white or light coloured detergent composition. Also, sometimes the increased proportion of insolubles in the detergent composition may be disadvantageous, possibly causing a lightening in the appearance of dark coloured laundry that has been washed with such a composition, and in other cases causing such a buildup of insoluble bentonite particles on the laundry as to make the laundry feel heavier and tactilely less satisfactory. Accordingly, research has been conducted in an effort to improve the effects of bentonite in laundry detergent compositions, with some aims of such research being to improve the softening effect of the bentonite on

fabrics washed with laundry detergent compositions containing it. By means of the present invention such objective has been achieved and additionally, improved fluffiness of washed laundry, such as all-cotton towels, has been noted.

In accordance with the present invention, a fabric softening and fabric fluffing particulate detergent composition comprises spray dried beads containing a deterative proportion of an anionic synthetic organic detergent or an ampholytic or amphoteric detergent which under the conditions of use act like an anionic detergent and a building proportion of a builder for such detergent, a fabric softening proportion of bentonite, which is capable of softening fabrics during washing thereof with the anionic detergent and builder, and a softening and fluffing proportion of a magnesium compound which is at least slightly water soluble, in such proportion that it improves the softening effect of the bentonite and improves the fluffiness of the fabrics washed with the detergent composition, which bentonite and magnesium salt are external to the spray dried beads of anionic synthetic organic detergent and builder, the composition being free of quaternary ammonium halide fabric softening cationic materials or containing only small proportions thereof and any such cationic materials present in the composition being located in separate particles from the anionic detergents, the composition being such that if the bentonite and magnesium compound are present as an agglomerate, the agglomerate is free of soap, and the said agglomerates are free of quaternary ammonium halide fabric softening cationic materials or optionally contain 0.1 to 3% thereof.

Various anionic detergents, usually as sodium salts, may be employed but those which are most

preferred are linear higher alkyl benzene sulphonates, higher alkyl sulphates and higher fatty alcohol polyethoxylate sulphates. Preferably, in the higher alkyl benzene sulphonate the higher alkyl is linear and of 12 to 15 carbon atoms, e.g., 12 or 13, and is a sodium salt. The alkyl sulphate is preferably a higher fatty alkyl (or higher fatty alcohol) sulphate of 10 to 18 carbon atoms, preferably 12 to 16 or 18 carbon atoms, e.g., 12, 16, and is also employed as the sodium salt. The higher alkyl polyethoxylate (or ethoxamer) sulphate anionic detergents will similarly be of 10 or 12 to 18 carbon atoms, e.g., 12, 18, in the higher alkyl group, which will preferably be a fatty alkyl group, and the ethoxy content will normally be from 3 to 30 ethoxy groups per mol, preferably 3 or 6 to 15 or 20. Again, the sodium salts are preferred. The alkyl groups are preferably linear or fatty higher alkyl groups of chain lengths within the 10 to 18 carbon atoms range, the cation is preferably sodium, and when a polyethoxy chain is present the sulphate is at the end thereof. Preferred anionic detergents are sodium linear tridecyl (or dodecyl) benzene sulphonate, sodium tallow alcohol sulphate and sodium tallow alcohol polyethoxylate sulphate wherein the polyethoxylate is of 6 to 15 ethylene oxide groups. Others that are also useful are the sodium higher olefin sulphonates and the sodium higher paraffin sulphonates. In addition to the anionic detergents mentioned, others of this well known group may also be present, especially in only minor proportions with respect to those previously described. Most such useful anionic detergents include an anionic base portion which includes a long chain alkyl group. Mixtures of anionic detergents may be employed and in some cases such

- mixtures can be superior to single detergents. The various anionic detergents 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, published in 1953 by Interscience Publishers, Inc. These and other anionic detergents are described by trade name and characteristics in the series of books issued under the title McCutcheon's Detergents and Emulsifiers, and specifically in the 1969 Annual.

- Instead of anionic detergents, amphoteric or ampholytic detergents may be employed providing that under the conditions of use they act like anionic products. Such detergents are also described in the Schwartz et al. text and in the already mentioned Detergents and Emulsifiers Annual.

- Although it is considered that anionic or anion-active detergents should be components of the present compositions for the desirable softening and fluffing effects to be obtained this does not mean that in addition to such detergents other deterative materials may not also be present. For example, higher fatty acid soaps, usually sodium soaps of fatty acids of 10 to 20 carbon atoms, preferably 12 to 18 carbon atoms, which may be made by neutralization of fatty acids or by neutralization of fats and oils, especially of mixtures thereof, may be present in the compositions of the present invention for their foam diminishing and deterative actions and it has been noted that the soaps,

- especially soaps like those of mixed tallow and coconut oil or hydrogenated tallow and coconut oil, with the ratios thereof being in the range of about 3:1 to 9:1 are especially good. Additionally,
5. nonionic detergents may be present with the anion-active deterative materials and in some instances small proportions of cationic detergents may be also be employed. The cationic detergents, which have softening activities in their own right,
 10. are preferably quaternary ammonium salts, e.g., dimethyl dilauryl benzylammonium chloride or cetyl trimethyl ammonium bromide. However, the cationic detergents are in separate particles from the anionic detergents to limit any undesirable
 15. interactions, and are processed in such a manner as not to be in intimate contact with the anionic detergents, also to limit such reactions. Of the nonionic detergents, which are also described in the texts previously mentioned (and the cationic
 20. detergents are also listed therein), most preferable are condensation products of ethylene oxide and propylene oxide with each other or with
 25. hydroxy-containing compounds, such as higher fatty alcohols (although higher alkyl phenols, such as nonyl phenols, and Oxo-type alcohols may also be used). In the preferred products the higher fatty alcohols are 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
 30. groups per mol, preferably from 6 to 12 or 15. More

- preferably, the nonionic detergent will be one in which the higher fatty alcohol is of about 12 to 13 or 15 carbon atoms and which contains about 6, 6.5, 7 or 11 moles of ethylene oxide. Among such
5. detergents are those made by Shell Chemical Company, available under the trade names Neodol (Registered Trade Mark) 23-6.5 and 25-7. Among their especially attractive properties, in addition to good
 10. 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 quickly solidifies. Such nonionic detergents may be incorporated in limited proportion, e.g., 2 to 4%,
 15. in a crutcher mix from which spray dried built detergent beads are made, or may be post-sprayed in liquid state onto tumbling base beads (with larger proportions of the nonionic detergent then being feasible).
 20. The builders that improve the detergency of the synthetic organic detergent (and often also improve the detergency of the water soluble soaps that may be employed) may be either the more conventional water soluble builders or the water insoluble
 25. builders. Among the former, both inorganic and organic builders may be useful, most of which are salts, preferably alkali metal salts, e.g., sodium salts. Among the inorganic water soluble builders those of preference are the various phosphates,
 30. usually polyphosphates, such as tripolyphosphates

- and pyrophosphates, especially the former. For example, pentasodium tripolyphosphate and tetrasodium pyrophosphate may be used. Of course, carbonates, such as sodium carbonate, are useful
5. builders and may desirably be employed, alone or in conjunction with bicarbonates, such as sodium bicarbonate. Sodium sesquicarbonate may be utilized instead of such carbonates. Other water soluble inorganic builders which are considered to be
10. effective in the compositions of the present invention include various other phosphates, borates, e.g., borax, and silicates, e.g., sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.4. As the water soluble organic builders it is preferred to utilize
15. citrates, gluconates, phosphonates, nitrilotriacetates, aminodiacetates and ethylene diamine tetraacetates. Preferably, all such compounds are alkali metal salts and more preferably they are sodium salts.
20. Among the water insoluble builders the most acceptable are the zeolites, preferably synthetic zeolites of Type A, X or Y, although some natural zeolites and other synthetic zeolites may also be utilized. Of the synthetic zeolites Type 4A is most
25. preferred. Crystalline zeolites are considered to be more effective in the compositions of the present invention than the amorphous zeolites and usually it is preferred to employ hydrated or partially hydrated zeolites. These compounds are
30. excellent as hardness ion removers from hard water

- and serve effectively to build synthetic organic detergents, especially anionic synthetic organic detergents. Usually they will have calcium ion exchange capacities in the range of 200 to 400 or more milligram equivalents of calcium carbonate hardness per gram of the aluminosilicate, preferably 250 to 350 mg eq/g. Also, they will normally include up to 9 molar proportions of water of hydration, preferably about 2.5 to 6 such proportions. Such zeolite ultimate particle diameters will usually be in the range of 0.01 to 20 microns and the zeolite particles will be of sizes within the range of 100 to 400 mesh, preferably 140 to 325 mesh (U.S. Sieve Series No's.) which have openings 149 to 37 microns and 105 to 44 microns across respectively.

- In addition to the synthetic detergents and builders the particulate materials which, together with the agglomerated bentonite and magnesium compound, make up the detergent compositions of the present invention, may include some moisture and one or more adjuvants or mixtures thereof. Among the adjuvants may be mentioned fluorescent brighteners; pigments; inorganic filler salts; bead structure modifiers, e.g., sodium polyacrylate; colourants; bactericides; fungicides, flow promoting agents; enzymes; bleaches and perfumes. The more stable of such materials may often be mixed in with other components of the crutcher mix and may be spray dried. Those which are less stable may be

post-added, agglomerated or otherwise incorporated by manufacturing methods to which they are less sensitive. Thus, the more stable of the adjuvants may be components of the spray dried beads and the less stable thereof may be agglomerated with the bentonite and magnesium compound or may be otherwise post-added to the compositions of the present invention.

The bentonite utilized is preferably a Wyoming or western bentonite having a swelling capacity in the range of 3 to 20 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 trade mark Mineral Colloid, as industrial bentonites, by Benton Clay Company, an affiliate of Georgia Kaolin Co. Such materials were formerly marketed under the trade mark THIXO-JEL by such company. They are selectively mined and beneficiated bentonites, and those considered to be very useful are available as Mineral Colloid 101, etc., and correspond to those formerly sold as THIXO-JELs Nos. 1, 2, 3 and 4. These 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 (which has openings 74 microns across). Beneficiated Wyoming bentonite is

- preferred as a component of the compositions of the present invention but other bentonites are also useful, especially when they form only a minor proportion of the total bentonite used. Although it
5. is desirable to limit free moisture content, as mentioned, it is more important to make certain that the bentonite being employed includes enough moisture, most of which is considered to be present between adjacent plates of the bentonite, to
10. facilitate quick disintegration of the bentonite and any adjacent materials in the particles when such particles or detergent compositions containing them are brought into contact with water, such as when the detergent composition is added to the wash
15. water. It has been found that at least about 2%, preferably at least 3%, more preferably at least 4% and most preferably 5% or more, to about 8%, of water should be present in the bentonite initially, before it is admixed with the other bead components
20. in the crutcher, and such a proportion of moisture 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 compositions of the
25. present invention. Thus, it is preferred not to spray dry the bentonite with other detergent composition components. When the bentonite moisture content is too low the bentonite does not act to the extent that is possible to prevent any silicate-
30. zeolite agglomerates being formed and it also does

- not aid enough in disintegrating the beads in the wash water. Additionally, when the bentonite is of satisfactory moisture content it exhibits an exchangeable calcium oxide percentage in the range of about 1 to 1.8 and with respect to magnesium oxide such percentage will normally then be in the range of 0.04 to 0.41, which exchange capacity is desirable.

- In place of Mineral Colloid 101 or other commercial bentonite of the type previously mentioned there may also be employed an equivalent bentonite such as one supplied by Amercian Colloid Company. This product, which may be available in powdered or agglomerated form, will generally comprise at least 90% of montmorillonite, $65\% \pm 3\%$ of SiO_2 , $18\% \pm 3\%$ of Al_2O_3 , $3.5\% \pm 0.3\%$ of Fe_2O_3 , $2.4\% \pm 0.6\%$ of MgO , $2.5\% \pm 0.2\%$ of Na_2O , $0.5\% \pm 0.2\%$ of CaO and $5.5\% \pm 0.5\%$ of water of crystallization. The loss on ignition will be $11\% \pm 1\%$ and any soluble silicate, usually with a $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4, and present as a binding agent in the agglomerate, often will be limited to 2%.

- In powder form the bentonite may pass through or almost pass through a No. 200 or No. 325 sieve (which have openings of 74 and 44 microns across respectively) but in agglomerated form it will normally be between No. 10 and No. 140 sieve size (which have openings of 2000 and 105 microns across respectively), such as 30-100 (which have openings 590-149 microns across), preferably all or at least about 90% being within the No's. 10

to 100 (2000-149 microns) or 10 to 120 range (2000-125 microns) and preferably all being in the 40 to 100 (420-149 microns). Thus, a sieve test will preferably have 0% beads on a No. 30 sieve (590 microns) 75% minimum on a No. 80 sieve (177 microns) and no more than 10% through a No. 100 sieve (149 microns). The dispersibility of the product will be 1.5 minutes maximum, its swelling rate will be 20 millilitres per minute and its frangibility will be 20% maximum in 15 minutes and 25% maximum in 30 minutes, as measured by standard evaluation tests. The apparent density of such product will usually be less than 0.7 g/ml and preferably it will be approximately that of the spray dried beads, often 0.3 to 0.5 g/ml, to prevent excessive sifting when such agglomerates are blended with the spray dried beads. The physical properties mentioned above are those which are desirable for agglomerates made from either bentonite powder or from such a powder in which a magnesium compound has been incorporated.

Instead of the described bentonites other bentonites of comparable fabric softening properties may also be employed providing that they are improved in fabric softening characteristics by the magnesium compound in accordance with the present invention. Some bentonites which are not initially satisfactorily fabric softening may be improved by alkali treatment, as by treatment of Italian bentonite with sodium carbonate, and such materials are available as Laviosa clays. Such bentonites may be employed and do

- soften laundry when they are present in detergent compositions, but they have not been found to be as satisfactory as western or Wyoming bentonites, which are preferably employed in accordance with the present invention.
- 5.

- The magnesium compounds which are useful in the products of the present invention and which increase the fabric softening effects of fabric softening bentonite also make various laundry items fluffier, especially those made of cotton, (so that a stack of towels, for example, will be higher after being washed in a product of the present invention than when washed in a bentonite containing detergent composition which is such that an equivalent softness of laundry results after washing). The magnesium compound utilized is normally one which is characterized as being water soluble, although, as will be evident from the following discussion, magnesium compounds that are at least slightly water soluble may also be used. Thus, when 0.2%, for example, of a magnesium compound, such as a magnesium salt, e.g., magnesium sulphate, is present in a detergent composition which is employed at a concentration of 0.15% in wash water for an automatic washing machine, the concentration of the magnesium compound will be 0.0003% or three parts per million. Accordingly, providing that the magnesium compound dissolves to such an extent in the wash water it could be effective. Similarly, a magnesium compound which dissolves to the extent of
- 10.
- 15.
- 20.
- 25.
- 30.

- 30 parts per million in water could be dissolved to the extent of two grams per 65 litres (normal American washing machine capacity) and such concentration or approximately such concentration of such compound is considered to be preferred. Of course, if it is the magnesium ion that is important to produce the desired improvement in softening and fluffing of washed laundry the proportion of magnesium compounds may be adjusted to provide a desired magnesium ion concentration. However, for simplicity, and because it is considered that often the compounds can be used substantially interchangeably, the amounts, proportions or concentrations of anhydrous magnesium compounds employed will be referred to herein.
5. such compound is considered to be preferred. Of course, if it is the magnesium ion that is important to produce the desired improvement in softening and fluffing of washed laundry the proportion of magnesium compounds may be adjusted to provide a
10. desired magnesium ion concentration. However, for simplicity, and because it is considered that often the compounds can be used substantially interchangeably, the amounts, proportions or concentrations of anhydrous magnesium compounds
15. employed will be referred to herein.

- The most useful magnesium compounds which are at least slightly water soluble are magnesium salts and the readily water soluble (e.g. of a solubility of at least 10 g/l at room temperature) magnesium salts are preferred. Of these the best is considered to be magnesium sulphate, which may be employed in the anhydrous form, as the monohydrate, the heptahydrate or $\text{MgSO}_4 \cdot 2.5 \text{H}_2\text{O}$. Synthetic kieserite, such as is available from RAD Co., preferably ground to be between No's 80 and 100 U.S. Sieve Series (which have openings 177 to 149 microns across), is a preferred source of magnesium. Another useful source thereof is a 1:1 mixture of magnesium sulphate and sodium carbonate. Other very useful magnesium salts include magnesium acetate, magnesium citrate, magnesium chloride, magnesium bromide, magnesium nitrate and magnesium carbonate. The
20. are preferred. Of these the best is considered to be magnesium sulphate, which may be employed in the anhydrous form, as the monohydrate, the heptahydrate or $\text{MgSO}_4 \cdot 2.5 \text{H}_2\text{O}$. Synthetic kieserite, such as is available from RAD Co., preferably ground to be
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magnesium carbonate is preferably a basic magnesium carbonate, such as one of the formula $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot n \text{H}_2\text{O}$, wherein n equals 3 or 4.

- The compositions of the present invention will
5. usually comprise from 5 to 35% of anionic synthetic organic detergent, 10 to 80% of builder, 4 to 30% of bentonite, and 0.2 to 5% of magnesium compound. Preferred ranges are 8 to 25% of the anionic detergent, 25 to 60% of builder, 5 to 15 or 20% of
 10. bentonite and 1 to 3 or 4% of magnesium compound. Also preferably present is from 5 to 40% of inorganic filler salt, such as sodium sulphate. Thus, a detergent composition according to the present invention may comprise from 5 or 10 to 35%
 15. of sodium higher linear alkyl benzene sulphonate wherein the linear alkyl group is of 12 to 13 carbon atoms, 5 to 40% of builder e.g. sodium tripolyphosphate, 2 to 10% of sodium silicate, 5 to 20% of sodium carbonate, 5 to 40% of sodium sulphate, 5 to
 20. 15 or 20% of bentonite, 1 to 3 or 4% of magnesium sulphate and 4 to 15% of moisture. Moisture contents may be from 2 to 20% but normally will not be outside the 4 to 15% range and usually preferably will be from 5 to 12%. Generally, the detergent
 25. compositions will contain no more than about 30% of adjuvants but when both sodium sulphate and sodium perborate are present in the final compositions (with the perborate normally being in distinct particulate form) higher proportions, up to 50% or
 30. 60%, may be employed. Generally, when no perborate or other sensitive bleach is present the adjuvants

will be limited to about 30% and when the sodium sulphate content is minimized the adjuvants may be held to 10%, e.g. 1 to 10%.

The above proportions of components are with respect to detergent compositions containing bentonite and magnesium compound. In such compositions the major proportion of material is in spray dried bead form, with the bentonite and magnesium compound being external to such beads. Thus, powdered or beaded bentonite and powdered or beaded magnesium compound may be mixed with the spray dried detergent-builder beads and with any other adjuvants desired but very preferably the bentonite and the magnesium compound will be agglomerated together into beads or particles to be mixed with the other particles. Such mixtures of beads are aesthetically desirable and are functionally superior because sifting on transportation and in storage is limited.

In the bentonite-magnesium compound agglomerates the proportion of bentonite to magnesium compound will be such that upon addition of the agglomerate to the spray dried beads of other components of the detergent composition the end product will be of a formula such as those previously described, in which the bentonite will exert a softening effect and the magnesium compound will improve such softening effect and improve the fluffiness of fabrics washed with the detergent composition. Such proportion of bentonite to magnesium compound, by weight, will

- usually be within the range of 20:1 to 1:1 or 1:2, preferably 10:1 to 2:1 and more preferably 6:1 to 3:1. The percentage of such agglomerate in the final detergent product will normally be within the
5. range of 4 to 50%, preferably 6 to 30% and more preferably 8 to 25%.

- The bulk density of the detergent product, often in the range of 0.25 to 0.65 g/ml, will preferably be such that the amount to be employed in standard
10. automatic washing machine operations will be conveniently measurable volumetrically. Thus, when the density is 0.34 g/ml, 1 1/4 cup (1.25 cups) of product will weigh 100 grams and if that amount is employed per wash the washing concentration of the
15. detergent composition will be the desired 0.15%. Similarly, if the bulk density is 0.43% g/ml only one cup (80 grams) of the detergent composition need be employed to obtain the same concentration. Of course, hand washing concentrations of the detergent
20. composition will usually be appreciably more, normally being from 0.15 to 0.5%, whereas machine washing concentrations will usually be from 0.05% (in some applications) to 0.2%.

- The bentonite-magnesium compound agglomerates
25. will normally comprise about 7 to 64% of magnesium compound (anhydrous basis), 26 to 87% of bentonite and 4 to 15% of moisture, with 0.5 to 5% of a binder preferably being present to assist in maintaining the integrity of the agglomerate until it is added
30. to water, in which it is readily disintegrable and

- dispersible. Preferably, the magnesium compound is magnesium sulphate, which may be added as synthetic kieserite, preferably of particle size in the 80 - 100 mesh range, or as epsom salt, and the binder is
5. sodium silicate, preferably of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.6 to 1:3, e.g. about 1:2.4. In such compositions the proportions of the magnesium sulphate, bentonite, sodium silicate and moisture are about 10 to 30%, 60 to 80%, 1 to 3%, and 5 to
 10. 12%, respectively, and the agglomerate particles are of sizes within the range of No's. 10 to 100 (2000 - 149 microns) or 120 (125 microns), U.S. Sieve Series, preferably 30 to 100 (590 - 149 microns). The above proportions of bentonite and magnesium compound may
 15. also be employed when such materials are dry mixed together and such mixture is then admixed with the other detergent component beads, or when the different materials are separately admixed with such beads, whether or not the bentonite and/or magnesium
 20. compound or mixture of such compounds are/is previously agglomerated. In a modification of the formula of the agglomerate a quaternary ammonium salt softening agent, such as distearyl dimethyl ammonium chloride, may be incorporated in the
 25. agglomerate to the extent of 0.1 to 3% as a softening and anti-static agent (to prevent cling of laundry after washing and machine drying).

- The bentonite-magnesium compound agglomerates may be made by spraying water or an aqueous solution
30. of a binder onto moving surfaces of the bentonite

- and the magnesium compound, which have been pre-mixed, and keeping the particles in motion until a major proportion thereof is agglomerated so as to be within a desirable size range. When that happens
5. the moisture content of the agglomerate may be in the range of about 20 to 40% and the binder content, if present, as is preferable, will be about 1 to 5% when its concentration in the mobile aqueous spray solution employed is in the range of about 2 to
10. 20%. The spray will usually contain 0.5 to 20% of binder, preferably 2 to 10% thereof. The binder concentration in the agglomerate will frequently be from 0.5 to 10%, e.g. 1 to 3%, when the binder is sodium silicate. The moisture content of the
15. agglomerated particles, as a result of the spraying onto them of the binder solution or dispersion, will normally be higher than desired initially but when anhydrous magnesium sulphate, for instance, is employed, the heat of hydration will help to drive
20. off some of the moisture. If the final moisture content is too high it may be lowered to the desired range of about 4 to 15%, preferably to a level about the same as the desired moisture content of the final detergent composition, by conventional
25. drying means, such as a fluid bed dryer.
- The binding spray solution employed will often be at an elevated temperature, such as in the range of 65 to 85°C but room temperature spraying is also feasible. The spray will be in finely divided
30. droplet form and will preferably be directed

transversely onto a moving screen of particles in the agglomerator.

- Various apparatuses may be used to carry out the agglomeration but that which is most preferred is an
5. O'Brien agglomerator. However, other means, such as the simpler inclined drum agglomerators may also be employed. The residence time in the agglomerator, whether operated continuously or as a batch, will usually be within the range of 10 to 30 minutes but
10. this depends on the design and operation of the agglomerator, as will be apparent to those skilled in this art.

- The spray dried beads of anionic detergent and builder, together with other components which may be
15. present therein, such as suitable adjuvants, are made by conventional spray drying methods. Thus, an aqueous crutcher mix comprising the anionic detergent, such as sodium higher linear alkylbenzene sulphonate wherein the linear alkyl group is of 12
20. to 13 carbon atoms, the builder or a mixture of builders, such as sodium tripolyphosphate, sodium silicate and sodium carbonate, with sodium sulphate as a filler, at a 40 to 70% solids concentration, and at a temperature of 50 to 70°C, may be crutched
25. for sufficient time to make the mix uniform, usually from 5 to 30 minutes, after which it is spray dried by being pumped through spray nozzles of a conventional countercurrent spray drying tower in which heated drying air (products of combustion of
30. oil or gas) at an inlet temperature of about 400 to

- 600°C drives off enough of the moisture content of the sprayed droplets of the crutcher mix to form the desired beads. The beads resulting will preferably be substantially in the No's. 10 120 range (or
5. 10-100) but may be and often are screened to such range(s). The beads will be satisfactorily free flowing at the desired moisture content thereof, which will usually be within the 4 to 15% range.

- After manufacture of the spray dried detergent-
10. builder beads and agglomeration of the bentonite-magnesium compound beads these may be mixed together with conventional blending equipment, such as a Day mixer or other suitable blender, after which the product may then be packaged and shipped or sent to
15. storage pending shipment.

- The fabric softening agglomerates of the present invention are useful for addition to conventional detergent compositions to improve the fabric softening and fabric fluffing properties thereof.
20. Thus, a conventional detergent composition may be transformed into a fabric softening and fluffing detergent product by mere mixing with the described agglomerate beads in a suitable proportion. The fabric softening and fluffing detergent compositions
25. of the present invention represent significant advances in the detergent art because they significantly improve fabric softening and do it with less of the fabric softening bentonite being required. Thus, the relatively small proportion of
30. magnesium compound, such as magnesium sulphate,

- which is present, significantly increases the fabric softening action of the bentonite, often to an extent that would otherwise require twice the bentonite content. This permits the production of
5. detergent compositions which are less chalky or milky in aqueous solution and could tend less to cause objectionable whitening of dark coloured fabrics. In addition to improving softening qualities the relatively small proportion of magnesium compound
 10. acts to whiten the bentonite, making its appearance more attractive. In some instances the magnesium compound aids in evaporating excess moisture from the product during agglomeration and it has been observed that it promotes the breakup of the
 15. agglomerate when the detergent composition is added to the wash water. Additionally, the magnesium compound, especially the sulphate, contributes to the fluffing effect of the compositions, making washed laundry, such as cotton towels, fluffier, so
 20. that a stack of towels, after five washings with the detergent composition of the present invention, will be higher than a stack after washings with a composition of comparable formula but containing no magnesium sulphate and containing enough bentonite
 25. to achieve equivalent softening effects. When bentonite and/or magnesium compound are/is added in the crutcher and formed into the spray dried beads the desirable improvement in softening and fluffing are not obtained to such a significant extent, if at
 30. all, and if other metal salts than that of magnesium

- are used with bentonite such improvements do not result. Also, the presence of a quaternary ammonium halide softening agent in the agglomerate, which is optional, will further help to soften the laundry and make it less susceptible to static and the quaternary ammonium compound does not deteriorate in manufacture or on storage because it is not objectionably reactive with the magnesium compound or the bentonite. Of course, if the quaternary ammonium halide softener had been added to the crutcher or was kept in intimate contact with anionic detergent it would deteriorate and its softening and anti-static effects would be lost.

- The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the following examples. Unless otherwise indicated, all parts are by weight and all temperatures are in °C.

20. EXAMPLES 1A to 1F
EXAMPLE 1A This is a comparison example.

	<u>Percent</u>
Sodium tridecylbenzene sulphonate	15.0
Sodium tripolyphosphate	32.0
25. Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$)	7.0
Sodium carbonate	17.0
Sodium sulphate	13.0
Adjuvants	2.0
Moisture	<u>9.0</u>
30.	100.0

- A 60% solids aqueous crutcher mix is made of the above components in the given proportions of solids so that on spray drying the beads resulting will be of the formula given. The crutcher mix is mixed for
5. a period of about 20 minutes at a temperature of about 70°C and is dried in a countercurrent spray drying tower to which the drying air is admitted at a temperature of about 450°C and into which the mix is pumped at high pressure through conventional
10. spray nozzles. The resulting beads are screened so as to be in the particle size range of No's. 10 to 100, U.S. Sieve Series (2000 to 149 microns).

EXAMPLE 1B.

- A commercial swelling bentonite, found to be
15. useful as a detergent composition fabric softener, which is sold under the trade name Mineral Colloid 101, as a finely divided powder of particle sizes about No. 325, U.S. Sieve Series (44 microns), is agglomerated in a 1:1 ratio with anhydrous magnesium
20. sulphate. To effect the agglomeration a mixture of both finely divided powders is made in the given proportion and while it is being tumbled in an inclined drum agglomerator (or an O'Brien agglomerator) deionized water is sprayed onto a
25. falling curtain of the mixture, created in the agglomerator. The spraying of the water onto the tumbling mixture of powders and the tumbling are continued until the desired extent of agglomeration is obtained. After the particles have reached the
30. desired size range they are dried to the desired

- moisture content, about 10%, in a fluidized bed dryer or other suitable dryer. The agglomerate resulting is next screened to the desired particle sizes, in the No's. 10 to 100 sieve range, and is ready for blending with the spray dried detergent composition beads to make an improved composition that softens and fluffs washed laundry. Analysis of the agglomerate indicates a content of about 45% of each of the bentonite and magnesium sulphate and about 10% of moisture. The spray dried detergent beads of Example 1A and the bentonite/magnesium sulphate agglomerate are then blended together in a suitable mixer, such as Day mixer or a V- or twin shell blender in a 5:1 proportion of detergent beads to agglomerate beads.
- 5.
 - 10.
 - 15.

- The detergent composition resulting is noted to appear whiter than when agglomerates of bentonite alone are used, which is considered to be desirable. The composition is then tested for softening activity, using a General Electric Company washing machine, with water at a hardness of 100 p.p.m., as calcium carbonate, and at a temperature of 49°C. The concentration of the detergent composition is 0.13% in the wash water and after completion of normal washing the washed material is dried in a laundry dryer.
- 20.
 - 25.

- A test towel that is washed and dried in accordance with the described procedure is evaluated for softness by an expert, who follows an evaluation procedure by which softness of laundry is rated on a
- 30.

scale from 1 to 10, with 10 representing the softest laundry. On such a scale the washed and dried towel is given a softness rating of 9.

EXAMPLE 1C. This is a comparison example.

5. When the same experiment is repeated, with a different but essentially identical towel being washed with a dry blend of five parts of the spray dried detergent composition and one part of Mineral Colloid 101, without the magnesium sulphate, the
10. softness rating given is 8.

EXAMPLE 1D. This is a comparison example.

- When the immediately preceding test is repeated except for cutting the amount of Mineral Colloid 101 in half in the dry blend (and using 0.15% of the
15. blend in the wash water) the softness rating is 7.

When the Mineral Colloid is omitted entirely (as in Example 1A) (or when the agglomerate of the present invention (Example 1B) is omitted) and the concentration is 0.15% the softness rating is 1.

20. Softness ratings of 9 and 10 are recognizable as significantly superior to ratings of 8 and 7 and it is considered that commercial products with such higher ratings achieve higher acceptance for softening effects by consumers.

25. The towel washed with the product of Example 1B, which had a softness rating of 9, is also noticeably fluffier than the other towels, which were washed with the other products. When the test is modified by having the washed towel line dried instead of
30. having it dried in an automatic laundry dryer greater

differences between the composition of Example 13 and the modifications thereof (Examples 1A, 1C, and 1D) will be noted and the composition of Example 13 will be even more significantly preferred.

5. EXAMPLE 1E.

When the swelling bentonite of Example 13 is replaced by an equivalent swelling bentonite sold under the name American Colloid Bentonite Clay, essentially the same results are obtained.

10. EXAMPLE 1F.

When however, a sodium carbonate-treated Italian or European bentonite, sold under the name Laviosa clay, is substituted for the Mineral Colloid 101, somewhat poorer results are obtained, although such results are relatively similar.

15. The above-reported examples may also be varied by using a 5% sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4) solution in water as the spray for spraying onto the mixture of bentonite and magnesium compound, with the spray being heated to a temperature of about 65°C and with the amount of sodium silicate in the agglomerate resulting being about 2% (Examples 2A to 2F).

20. Instead of the sodium silicate solution, similar solutions of other binding agents, such as polyvinyl alcohol (Examples 3A to 3F), sodium carboxymethyl cellulose (Examples 4A to 4F), polyvinyl pyrrolidone (Examples 5A to 5F) and hydroxyethyl cellulose (Examples 6A to 6F), may be used to improve the physical strength of the agglomerate and prevent

25.

30.

- disintegration thereof. When the agglomerate containing binder is tested for softness and fluffiness the detergent composition containing the agglomerate of bentonite and magnesium compound is still superior to compositions of the other types previously described (except for other bentonite - magnesium compound agglomerates). Such is also the case when the agglomerates are of particle sizes in the No's., 30-100 range, U.S. Sieve Series.

10. EXAMPLES 7-12

- When instead of anhydrous magnesium sulphate, RAD Co. synthetic kieserite (Examples 7A to 7F), epsom salt (Examples 8A to 8F) or other magnesium sulphate hydrate is utilized or when magnesium acetate (Examples 9A to 9F), basic magnesium carbonate (Examples 10A to 10F), magnesium chloride (Examples 11A to 11F), magnesium nitrate (Examples 12A to 12F) or other at least slightly soluble magnesium compound is employed, completely or partially in replacement of the magnesium sulphate in the described agglomerates with the bentonite (although it is preferred to use those of a solubility of at least 10 g/l in room temperature water), improved softening (and fluffiness) of washed fabrics (such as cotton towels) result, compared to similar formulations containing more bentonite but no magnesium compound with the agglomerate. When the same proportions of bentonite and magnesium compound are dry blended with the spray dried beads softening and fluffing results,

- measured on fabrics washed with such compositions, are about the same as or almost as good as those utilizing the agglomerates but the products tend to segregate on shipping and storage and the softening effects are not uniform for all of the product in the box of detergent composition. Also, the appearance of the product is not as acceptable aesthetically and the presence of fine powdered material with the detergent beads is considered undesirable by consumers.

EXAMPLE 13

- When 1 or 2%, on a product basis, of distearyl dimethyl ammonium chloride, an anti-static and fabric softening agent, is included in the agglomerate of the present invention, by being dissolved and/or dispersed in the binder solution or by being otherwise mixed in with the agglomerate, its anti-static action on washed laundry is apparent, especially when that laundry includes synthetic organic polymeric fibrous materials, such as nylons and polyesters, and it is considered that it further helps to soften cottons in the laundry.

EXAMPLES 14 and 15

- Good results are obtained in accordance with the invention by substituting other anionic detergents, such as sodium lauryl sulphate (Example 14) and polyethoxylated sodium cetyl sulphate containing about 10 moles of ethylene oxide per mole (Example 15), for the sodium tridecylbenzene sulphonate.

EXAMPLES 16, 17 and 18

- Similarly, substituting other builders, such as tetrasodium pyrophosphate (Example 16), sodium sesquicarbonate (Example 17) and NTA (Example 18) results in generally the same desirable properties in the product.

- Such is also the case when the proportions of the various components are varied $\pm 10\%$, $\pm 20\%$ and $\pm 30\%$, providing that they remain within the ranges given. Of course, all the products described are useful synthetic organic detergents for washing laundry and all clean the laundry satisfactorily.

EXAMPLES 19A to 19C

EXAMPLE 19A. This is a comparison example.

	<u>Percent</u>
15. Sodium dodecylbenzene sulphonate	19.9
Sodium tripolyphosphate	27.7
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$)	10.5
Sodium carbonate	17.3
20. Sodium sulphate	15.4
Fluorescent brightener (Tinopal (Registered Trade Mark) CBS-X)	0.1
Moisture	<u>9.1</u>
	100.0

25. Spray dried detergent-builder beads of the above formula are made by essentially the same spray drying method described in Example 1A. The beads are of particle sizes in the 10-100 sieve range.

EXAMPLE 19B

30. An agglomerate of American Colloid Bentonite Clay and anhydrous magnesium sulphate is made by dry

- mixing such materials in an inclined drum agglomerator, with the ratio of the bentonite to the magnesium compound being 4:1, the mixture thereof is oversprayed with a dilute (5%) sodium silicate solution in the manner described in Example 13 and agglomerates are formed. The agglomerates are dried to a final moisture content of about 10% and are sieved so that they pass through a No. 40 sieve (420 microns) and rest on a No. 100 sieve (149 microns).
5. The final sodium silicate content of the agglomerates varies but it is usually within the range of 1 to 3%, e.g. 2%.
- 10.

- The spray dried detergent beads of Example 19A, the bentonite-magnesium compound agglomerate and borax dots (puffed borax coloured with Acid Blue 80) are then dry blended together, with the percentages thereof in the blend being 87%, 12% and 1%, respectively.
- 15.

- The product resulting is an attractive, free-flowing fabric softening and fluffing detergent composition which, when used at a concentration of 0.15% in the wash water of an automatic washing machine (100 g/ 65 l of water) is an excellent detergent of very satisfactory softening characteristics and good cotton fluffing properties.
- 20.
- 25.

EXAMPLE 19C

- When the crutcher mix of Example 19A is changed so as to include hydrated Zeolite 4A (20% hydration water) in place of the sodium tripolyphosphate, and sodium bicarbonate in place of some (1/4 to 3/4) of
- 30.

the sodium carbonate of the formula a satisfactory non-phosphate softening detergent composition results. Also, when mixtures of Zeolite 4A and other builders, such as sodium sesquicarbonate or equal weight mixtures of sodium bicarbonate and sodium carbonate are utilized with the zeolite, or when other zeolites which remove calcium from hard water, such as other Zeolites A and Zeolites X and Y are employed, similar good results are obtainable when the agglomerate of Example 19B is used.

The excellent fabric softening is especially noted when the laundry is of cotton and such results are obtainable using others of the described anionic synthetic organic detergents (which may be accompanied by nonionic detergents or amphoteric detergents), builders, bentonites and magnesium compounds and when the proportions of the required components of the compositions are varied but are still within the mentioned ranges. A preferred substitute builder is tetrasodium pyrophosphate, which may be used alone or with sodium tripolyphosphate. Also, various adjuvants, such as fluorescent brighteners, colourants, germicides and anti-redeposition agents, may be added in the crutcher and different fillers or no filler may be present in the crutcher mix (and in the spray dried beads). Among adjuvants that may be present in the bentonite/magnesium compound agglomerate are perfumes, enzymes, soil release promoting agents, and other heat-sensitive products. Of course, as with the case of the borax dots, materials may be present in the final composition external to both the spray dried beads and the agglomerates, which materials may be agglomerates, prills or powders. Among such materials are bleaches, such as sodium perborate,

and enzymes, and perfumes may be sprayed onto the mixture of detergent beads and agglomerates. Such modifications of the final products, and processes for their manufacture still permit the obtaining of the improved softening and fluffing results previously mentioned.

As indicated in Example 1, when only bentonite is present in the detergent composition (magnesium compound omitted) (comparison Example 1C) but the compositions are otherwise like those of this example, the products of the present invention soften laundry better and additionally, make it fluffier than do the products of this comparison Example 1C. This is so even when the amount of bentonite in Example 1C is increased to replace the magnesium compound.

EXAMPLE 20A

A commercial heavy duty laundry detergent (FAB (Registered Trade Mark)), based on sodium linear higher alkylbenzene sulphonate wherein the alkyl group is of 13 carbon atoms, and sodium tripolyphosphate, with sodium sulphate as a filler and containing moisture, with the percentages of synthetic organic detergent, builder, filler, moisture and other adjuvants being about 15, 55, 20, 9 and 1, is improved with respect to fabric softening effect by mixing the beads thereof with an agglomerate of equal parts of Thixo-Jel No. 1 (bentonite) and MgSO_4 . Manufacture of the agglomerate is by essentially the same method as was

- previously described, wherein silicate is used to improve bead strength. The blend made is of five parts of the FAB (Registered Trade Mark) to one part of the agglomerate. Washing in an automatic washing machine is conducted at a 0.15% FAB (Registered Trade Mark) concentration (total composition concentration being 0.18%), with the water being at 21°C and of 100 p.p.m. hardness (as calcium carbonate). The test laundry washed in the laboratory in a washing machine includes two cotton face cloths and after washing such are line dried. They are then evaluated for softness in the manner previously described and are given a rating of 9.

EXAMPLE 20B. This is a comparison example.

- When the above Example 20A is repeated, using one part of agglomerated Thixo-Jel with the FAB in replacement of the Thixo-Jel - MgSO_4 agglomerate, the softness rating obtained is 8. When both such experiments are repeated using wash water at a temperature of 49°C, the same results are obtained.

- In similar tests employing six pound (2.7 Kg) clean loads of laundry in which there are present three face cloths, with the FAB (Registered Trade Mark) concentration being 0.15% in 20°C wash water of 100 p.p.m. hardness, as calcium carbonate, agglomerates containing two parts of MgSO_4 and ten parts of bentonite are made and are blended with 100 parts of the FAB (Registered Trade Mark) (to give a wash water concentration of 0.17%). When the bentonite is Thixo-Jel No. 1 each face cloth is rated 9 for softness and is found to be very fluffy, and the same is true when the bentonite is American Colloid Bentonite Clay.

EXAMPLE 21

- A commercial American heavy duty laundry detergent (FAB (Registered Trade Mark)) is made into a softening and fluffing detergent by addition thereto
5. of 12 parts per hundred of an agglomerate of American Colloid Bentonite Clay and MgSO_4 (4:1 ratio). The magnesium sulphate employed in three variations of this experiment is in anhydrous form, is crystals of monohydrate and is finely ground
10. crystals of the monohydrate. In another experiment instead of an agglomerate being used, the magnesium sulphate monohydrate crystals, of particle sizes like those of the FAB (Registered Trade Mark), are dry blended with agglomerated American Colloid
15. Bentonite Clay (which does not contain any MgSO_4). All four of these variations of the present invention are compared for fabric softening activity to 100 parts of FAB plus 20 parts of agglomerated American Colloid Bentonite Clay.
20. Cotton cloths washed with the "control" are rated 8 for softness and cloths washed in the compositions containing the agglomerates of the present invention are rated 9, which difference is considered to be very significant. The composition
25. made with the dry blend of MgSO_4 (monohydrate) and bentonite is rated 7.

EXAMPLE 22

- To simulate European-type detergent compositions a heavy duty detergent composition is made by
30. blending 10 parts of sodium linear tridecylbenzene sulphonate (derived from FAB), 5 parts sodium coco-

tallow soap (20:80 ratio), 32 parts of sodium tripolyphosphate and 25 parts of sodium perborate. To 100 parts of such product are added 12 parts of an agglomerate of 5 parts of American Colloid

5. Bentonite Clay and 1 part of $MgSO_4$.

The described composition is tested for softening power in a Miele (Registered Trade Mark) washing machine, using wash water of a hardness of 300 p.p.m., as calcium carbonate, and employing 100

10. grams of the detergent composition per wash, with six pound (2.7 Kg) clean loads being washed. The washing is conducted with water at a temperature of $60^{\circ}C$ and after completion of the washing the dried laundry (cotton) is evaluated for softness and is
15. given a softness rating of 9. It is also noted that apparently due to the presence of the soap the amount of foaming that would normally be expected from the sodium tridecylbenzene sulphonate is greatly diminished, thereby aiding the washing
20. effect. Despite the presence of the soap, which might be expected to react with the magnesium compound to form insoluble soap, which has a lesser effect in softening laundry, the high softness rating is obtained.

25. The above examples show that the agglomerates of bentonite and magnesium compound of the present invention, when incorporated with anionic detergent-based detergent compositions, are effective detergents, significantly improve the softening power of
30. such compositions and improve the desirable fluffiness of the laundry. The compositions also are

good whitening agents and help to remove stains from fabric substrates. With respect to fluffiness, in some cases it has been noted that stacked towels are as much as 43% higher than towels of similar

5. softness washed with compositions wherein only bentonite is the softening agent.

In addition to machine washing of laundry it is also considered that the products of the present invention are useful as detergent compositions for

10. hand washing (and line drying) laundry. The concentrations thereof in the wash water will be higher, often being from 0.2 to 1%, e.g. 0.35%, 0.7%, but the softenings are usually not as good as when a washing machine is used. Still, the composi-
15. tions of the present invention are more effective softeners than those from which the magnesium compound is omitted.

CLAIMS

1. A fabric softening and fabric fluffing particulate detergent composition which comprises spray dried beads containing a deterative proportion of an anionic synthetic organic detergent or an ampholytic or amphoteric detergent which under the conditions of use act like an anionic detergent and a building proportion of a builder for such detergent, a fabric softening proportion of bentonite, which is capable of softening fabric during washing thereof with the anionic detergent and builder, and a softening and fluffing proportion of a magnesium compound which is at least slightly water soluble, in such proportion that it improves the softening effect of the bentonite and improves the fluffiness of the fabrics washed with the detergent composition, which bentonite and magnesium compound are external to the spray dried beads of anionic synthetic organic detergent and builder, the composition being free of quaternary ammonium halide fabric softening cationic materials or containing only small proportions thereof and any such cationic materials present in the composition being located in separate particles from the anionic detergents, the composition being such that if the bentonite and magnesium compound are present as an agglomerate, the agglomerate is free of soap, and the said agglomerates are free of quaternary ammonium halide fabric softening cationic materials or optionally contain 0.1 to 3% thereof.

2. A detergent composition as claimed in Claim 1 in which the bentonite is in the form of an agglomerate which disintegrates readily in wash water.



3. A detergent composition as claimed in Claim 2 in which the magnesium compound is magnesium salt and is present with bentonite in at least a portion of the bentonite agglomerate.

4. A detergent composition as claimed in Claim 1 in which the anionic synthetic organic detergent and builder (which may be a mixture of builders) are in the form of spray dried beads, and the bentonite and magnesium compound (which may be magnesium sulphate) are agglomerated to particles of about the same size as the spray dried beads of anionic synthetic organic detergent and builder.

5. A detergent composition as claimed in any one of Claims 1 to 4 which comprises 5 to 35% of anionic synthetic organic detergent, 10 to 80% of builder, 4 to 30% of bentonite, and 0.2 to 5% of magnesium salt.

6. A detergent composition as claimed in any one of Claims 1 to 5 in which there is 1-4% of magnesium compound.

7. A detergent composition as claimed in any one of Claims 1 to 6 in which the magnesium compound is magnesium sulphate.

8. A detergent composition as claimed in any one of Claims 1 to 7 in which the magnesium compound is magnesium sulphate, 1 to 4% thereof is present in the composition, and it is distributed evenly in all the bentonite agglomerate.



9. A detergent composition as claimed in any one of Claims 1 to 7 in which the bentonite and the magnesium compound are present as an agglomerate.
5. 10. A detergent composition as claimed in Claim 9 in which the agglomerates have a particle size in the range 10-120 mesh U.S. Sieve Series (which have openings 2000 to 125 microns across).
10. 11. A detergent composition as claimed in Claim 9 in which the agglomerates have a particle size in the range 30-100 mesh U.S. Sieve Series (590-149 microns).
15. 12. A detergent composition as claimed in Claim 8, 9 or 10 in which the proportion of magnesium compound to bentonite in the magnesium compound-bentonite agglomerate is from 1:20 to 1:1.
20. 13. A detergent composition as claimed in any one of Claims 1 to 12 comprising from 5 to 35% of sodium higher linear alkylbenzene sulphonate wherein the linear alkyl group is of 12 to 13 carbon atoms, 5 to 40% of builder, 2 to 10% of sodium silicate, 5 to 20% of sodium carbonate, 5 to 40% of sodium sulphate, 5 to 20% of bentonite, 1 to 4% of magnesium sulphate and 4 to 15% of moisture.
25. 14. A detergent composition as claimed in Claim 13 in which the builder is sodium tripolyphosphate.
- 30.



15. A detergent composition as claimed in any one of Claims 1 to 13 in which the builder is a water softening and calcium ion exchanging zeolite.
5. 16. A detergent composition as claimed in any one of Claims 1 to 14 in which the spray dried beads are of particle sizes in the range 10 to 100 mesh U.S. Sieve Series (2000-149 microns).
10. 17. A detergent composition as claimed in any one of Claims 13 to 16 in which the sodium linear higher alkylbenzene sulphonate, sodium tripolyphosphate, sodium silicate, sodium carbonate and sodium sulphate are in spray dried bead form, of particle sizes in the No's. 10-100 range, U.S. Sieve Series, and the bentonite-magnesium sulphate agglomerates are of particle sizes in the No's. 30-100 range, include as a binding agent from 0.5 to 5%, on the basis of the agglomerate weight, of sodium silicate, and are of a moisture content in the range of 4 to 15%.
20. 18. A detergent composition as claimed in Claim 1 and substantially as specifically described herein with reference to any one of the examples B, E or F of Examples 1 to 12, Examples 13 to 18, Examples 19B or 19C, Example 20A, Example 21 or Example 22.
25. 19. A particulate fabric softening and fluffing composition suitable for incorporation in detergent compositions for softening and fluffing laundry washed with such compositions, which comprises
- 30.



- agglomerates of finely divided bentonite which is capable of softening fabrics during washing thereof with such detergent composition, and a magnesium compound which is at least slightly water soluble,
5. in such proportion that it improves the softening effect of the bentonite and improves the fluffiness of fabrics washed with the detergent composition, the agglomerate being free of soap, the said agglomerates being free of quaternary ammonium
10. halide fabric softening cationic materials or containing no more than 3% thereof.

20. An agglomerated fabric softening and fluffing composition as claimed in Claim 19 in which
15. the magnesium compound is magnesium sulphate.

21. A composition as claimed in Claim 19 or 20 which comprises about 7 to 64% of magnesium compound, 26 to 87% of bentonite, 0.5 to 5% of a
20. binder in the agglomerate to assist in maintaining the integrity of the agglomerate until it is added to water, in which it is readily disintegrable and dispersible, and 4 to 15% of moisture.

25. 22. A composition as claimed in any one of Claims 19 to 21 containing a binder in which the binder is sodium silicate.

23. A composition as claimed in Claim 21 or
30. Claim 22 in which the proportions of magnesium compound, bentonite, binder and moisture are about 10-30%, 60-80%, 1-3% and 5-12%, respectively.



24. A composition as claimed in any one of Claims 19 to 23 in which the agglomerate particles are of sizes within the range of No's. 10-120 U.S. Sieve Series (2000 to 125 microns).

5.

25. A composition as claimed in any one of Claims 19 to 24 containing a binder in which the binder is sodium silicate, the proportions of magnesium compound, bentonite, sodium silicate, and moisture are about 10 to 30%, 60 to 80%, 1 to 3% and 5 to 12%, respectively, and the particles are of sizes within the range of No's. 10-120, U.S. Sieve Series.

15. 26. A particulate fabric softening and fluffing composition as claimed in Claim 19 substantially as specifically described herein with reference to any one of the examples B, E or F of Examples 1 to 12, Examples 13 to 18, Examples 19B or 19C, Example 20A, 20. Example 21 or Example 22.

