

CLAY SALT FABRIC SOFTENING
PARTICULATE AGGLOMERATE, PROCESSES FOR
MANUFACTURE AND USE THEREOF, AND DETERGENT
COMPOSITIONS CONTAINING IT

5

The present invention relates to agglomerating particles of finely divided fabric softening clay such as bentonite and salt such as sodium sulphate. More particularly, it relates to such agglomerates wherein the proportion of salt is minor. Thus, the proportion of bentonite to sodium sulphate, both of which, before agglomeration, are in finely divided form, is in the range of 2:1 to 10:1, preferably 3:1 to 5:1.

15

In the synthetic organic detergent art it is recognised that certain smectite clays, such as bentonite, exhibit fabric softening properties when incorporated in or used with built synthetic organic detergent compositions. Such clays have been mixed with detergent composition components in the crutcher and have been spray dried with such components to make spray dried fabric softening particulate detergents. Instead of spray drying the fabric softening clay together with the other constituents of the detergent composition, it has sometimes been preferred to agglomerate the clay, often with the aid of a binding agent, such as sodium silicate, in aqueous solution, to make agglomerates of approximately the same size as spray dried detergent composition beads, so that the agglomerates may be mixed with the spray dried detergent beads to produce particulate fabric softening detergent compositions.

30

Our copending GB Application 8528757 Serial No. 2167460 published 29th May 1986 discloses bentonite sodium sulphate agglomerates and their use in detergent compositions but does not disclose their use in combination with water soluble copolymers of maleic and acrylic acids. According to the present invention a fabric softening particulate detergent composition comprises from 5 to 25% of synthetic anionic organic detergent, 20 to 60% of inorganic builder(s) for the detergent, 5 to 40% of water soluble inorganic filler salt, 4 to 18% of moisture, 0 to 5% of adjuvant(s), in spray dried bead form, a detergency improving proportion of a water soluble copolymer of maleic and acrylic acids optionally as a salt thereof, and 5 to 30% of fabric softening agglomerate of fabric softening clay and water soluble ionisable salt (other than silicate), which agglomerate comprises particles of sizes in the range of Nos. 10 to 140 sieves, U.S. Sieve Series, (which have openings 2000 to 105 microns across), which are agglomerates of mixtures of finely divided fabric softening clay and water soluble ionisable salt (other than silicate) with at least 50% by weight of each of the particles being less than No. 100 sieve size (which has openings 149 microns across), with the proportions of fabric softening clay and water soluble ionisable salt (other than silicate) being within the range of one part of salt by weight to 2 to 10 parts of clay by weight, with the clay and salt particles being held together in the agglomerate particles by hydrated clay at the surfaces of the

2a.

said particles, and with the agglomerate particles being of a moisture content in the range of 5 to 16% by weight.

5 Our divisional application no. 8824739 Serial
No. 2208665 divided out from the present application
is directed to a fabric softening clay, e.g bentonite-
sodium carbonate agglomerate comprising agglomerate
particles of sizes in the range of No's. 10 to 140
sieves, U.S. Sieve Series (which have openings 2000
10 to 105 microns across), which are agglomerates of

15

20

25

30

mixtures of finely divided clay and sodium carbonate, with at least a major proportion by weight of each of the bentonite and sodium carbonate particles being less than No. 100 sieve size (i.e. less than 149
5 microns across), with the proportions of clay and sodium carbonate being within the range of one part of sodium carbonate by weight to 2 to 10 parts of clay by weight, with the clay and sodium carbonate particles being held together in the agglomerate
10 particles by hydrated clay at the surfaces of the said particles, and with the agglomerate particles being of a moisture content in the range of 5 to 16% by weight.

The bentonite employed is a colloidal clay
15 (aluminium silicate) containing montmorillonite. Montmorillonite is a hydrated aluminium silicate in which about 1/6th of the aluminium atoms may be replaced with magnesium atoms and with which varying amounts of sodium, potassium, calcium, magnesium and
20 other metals, and hydrogen, may be loosely combined. The type of bentonite clay which is most useful in making the agglomerated particles of the present invention is that which is known as sodium bentonite (or Wyoming or western bentonite), which is normally
25 light to cream-coloured impalpable powder which, in water, forms a colloidal suspension having strongly thixotropic properties. In water the swelling capacity of the clay will often 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 often 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

5. 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 bentonites, and those considered to
10. be most useful are available as Mineral Colloid No's. 101, 102, 103 and 104, corresponding to THIXO-JEL's No's. 1, 2, 3 and 4. Such materials have pH's (at 6% concentration in water) in the range of 8 to 9.4, maximum free moisture contents of about 8% and
15. specific gravities of about 2.6, and for the pulverised grade at least about 85% (and preferably 100%) passes through a 200 mesh U.S. Sieve Series sieve (which has openings 74 microns across). More preferably, the bentonite is one wherein essentially
20. all the particles (over 90%, preferably over 95%) pass through a No. 325 sieve (which has openings 44 microns across) and most preferably all the particles pass through such a sieve. Beneficiated western or Wyoming bentonite is preferred as a component of the
25. compositions of the present invention, but other bentonites are also useful, especially when they form only a minor proportion of the bentonite used.

Although it is desirable to limit the maximum free moisture content, as mentioned, the bentonite

30. being employed should include enough free moisture,

- most of which is considered to be present between adjacent plates of the bentonite, to facilitate quick disintegration of the bentonite-salt agglomerate when such particles or detergent compositions containing
5. them are brought into contact with water, such as wash water. It has been found that at least about 2%, preferably at least 3% and more preferably, at least about 4% or more of water should be present in the bentonite initially, before it is agglomerated,
10. and such proportion should also be present after any drying. Overdrying to the point where the bentonite loses its "internal" moisture can diminish the utility of the compositions of the present invention apparently because when the bentonite moisture
15. content is too low the bentonite does not satisfactorily soften laundry by depositing on it from the wash water. When the bentonite is of satisfactory moisture content, and so is operative in the present invention, it can have an effective exchangeable
20. calcium oxide percentage in the range of about 1 to 1.8; with respect to magnesium oxide such percentage will often be in the range of 0.04 to 0.41. A typical chemical analysis of such a material is from
25. 64.8 to 73.0% of SiO_2 , 14 to 18% of Al_2O_3 , 1.6 to 2.7% of MgO , 1.3 to 3.1% of CaO , 2.3 to 3.4 of Fe_2O_3 , 0.8 to 2.8% of Na_2O and 0.4 to 7.0% of K_2O .

- Instead of utilising the THIXO-JEL or Mineral Colloid bentonites one may also employ equivalent competitive products, such as that sold by American
30. Colloid Company, Industrial Division, as General

- Purpose Bentonite Powder, 325 mesh, which has a minimum of 95% thereof finer than 325 mesh or 44 microns in diameter (wet particle size) and a minimum of 96% finer than 200 mesh or 74 microns in diameter (dry particles size). Such a hydrous aluminium silicate is comprised principally of montmorillonite (90% minimum), with smaller proportions of feldspar, biotite and selenite. A typical analysis, on an "anhydrous" basis, is 6.0% silica, 21.5% alumina, 3.3% of ferric iron (as Fe_2O_3), 0.4% of ferrous iron (as FeO), 2.7% of magnesium (as MgO), 2.6% of sodium and potassium (as Na_2O), 0.7% of calcium (as CaO), 5.6% of crystal water (as H_2O) and 0.7% of trace elements. Also useful is a product sold by American Colloid Company as AEG-325 mesh sodium bentonite.

- Although the western bentonites are preferred it is also possible to utilise synthetic bentonites, such as those which may be made by treating Italian or similar bentonites containing relatively small proportions of exchangeable monovalent metals (sodium and potassium) with alkaline materials, such as sodium carbonate, to increase the calcium ion exchange capacities of such products. Analysis of an Italian bentonite after alkali treatment shows it to contain 66.2% of SiO_2 , 17.9% of Al_2O_3 , 2.80% of MgO , 2.43% of Na_2O , 1.25% of Fe_2O_3 , 1.15% of CaO , 0.14% of TiO_2 and 0.13% of K_2O , on a dry basis. It is considered that the Na_2O content of the bentonite should be at least about 0.5%, preferably at least 1% and more preferably at least 2% (with the equivalent

- proportion of K_2O also taken into account), so that the clay will be satisfactorily swelling, with good softening and dispersing properties in aqueous suspension, to accomplish the purposes of the present invention. Preferred swelling bentonites of the synthetic types described are sold under the trade names Laviosa and Winkelmann, e.g., Laviosa AGB and Winkelmann G 13.

- The salt, which is employed with the bentonite in the agglomerate particles to increase fabric softening by the bentonite, is preferably anhydrous sodium sulphate, although partially hydrated sodium sulphate may also be useful in some applications. The anhydrous sodium sulphate has greater heats of solution and hydration and apparently such aid in quickly breaking up the agglomerate in the wash water. The ability of the bentonite to form a gel with water also aids in binding the components together in the desired agglomerates, with the hydrated particle surfaces cementing the particles together, and may aid in keeping the sulphate in anhydrous form in the agglomerate, which is considered to be desirable.

- The water employed is preferably of low hardness and inorganic salt contents but ordinary city waters may be used. Usually the hardness contents of such water will be less than 300 ppm, as calcium carbonate, preferably less than 150 ppm, as $CaCO_3$, and the water will be used as a spray.

- The agglomerating spray may also contain other

components, especially minor, non-interfering
adjuvants, which may desirably be incorporated with
the bentonite-salt agglomerates. For example, in
some instances dyes and/or pigments, such as Polar
5 Brilliant Blue and ultramarine blue, respectively,
may be employed, either dissolved or dispersed in the
spray liquid. Other materials that may sometimes be
present in the spray (or mixed with the powders)
include nonionic detergents, fluorescent brighteners,
10 perfumes, antibacterial compounds, sequestrants and
binders. Among binders that sometimes are useful may
be mentioned inorganic binders, such as sodium
silicate, and organic binders, such as gums, e.g.
sodium alginate, carrageenan, sodium carboxy-
15 methylcellulose and carob bean gum, gelatin, and
resins, such as polyvinyl alcohol and polyvinyl
acetate. However, it is a desirable and important
feature of the present invention that agglomerates of
satisfactory strength and ready dispersibility may be
20 made without the use of binders, with only water
being employed in the agglomerating spray and with
the adherence together of the component powders of
the agglomerates being effected by the self-cementing
actions of such components, which sometimes form
25 stable hydrates and/or gels in the presence of water,
to bind the powders together in agglomerates, and yet
to release them quickly in wash water so that they
will be dispersed immediately and will promptly
exercise their combined fabric softening function.

The finely powdered clay employed is of particle sizes less than No. 100 sieve, U.S. Sieve Series (which has openings 149 microns across), preferably less than No. 200 sieve (which has openings 74 microns across), more preferably with essentially all (over 90%) of the particles thereof passing through a No. 325 sieve (which has openings 44 microns across), and most preferably with all such particles passing through such sieve. A major proportion of the salt, e.g. sodium sulphate, particles to be agglomerated should be of particle sizes less than No. 100 sieve (which has openings 149 microns across) so as to be effective in improving the softening activity of the bentonite particles when the agglomerate is dispersed in an aqueous medium which is used to soften (and preferably also to wash) laundry. Preferably the particle sizes of the salt powder will be less than No. 200 sieve and ideally such particles will pass through a No. 325 sieve (or essentially all of them will pass through such a sieve).

While it is important to the effective operation of the present invention that the clay and salt particles be very finely divided, as indicated, it

should be recognised that good improvement of fabric softening is obtained when the clay and salt particles to be agglomerated are smaller than No. 100 sieve. Even when some such particles may be larger than No. 100 sieve the presence of a major proportion (by weight) of particles that pass a No. 100 sieve results in significant and noticeable improvement in softening laundry fabrics. Therefore, it is within the present invention to utilise finely divided clay and salt, for each of which at least 50% by weight is of particles less than No. 100 sieve.

In addition to the particle sizes of the clay and salt components of the present agglomerates being important it is also important that the proportion of clay and salt be within a relatively limited range, so as to obtain the desired improvement in the softening effect of the clay on the laundry. Thus, the agglomerate may be of 2 to 10 parts of bentonite, by weight, to one part of sodium sulphate. Preferably such proportion will be 3 to 5 parts to one and more preferably it will be 7 to 9 parts of bentonite to two parts of sodium sulphate. Still more preferably the ratio of bentonite to sodium sulphate will be about 4:1. Lesser proportions of sodium sulphate than 1:10 will not appreciably improve the bentonite fabric softening and when greater proportions of sulphate than 1:2 are present softening action is diminished.

The agglomerate made will be of a moisture

content in the range of 5 to 16% by weight, preferably 5 to 12%, and more preferably 6 to 10%. Such moisture contents, especially that which is more preferred, have been found to satisfactorily bind the components of the agglomerate together, so that they do not disintegrate on shipping and handling, and yet, make the agglomerates readily dispersible in wash water so that the full softening effect of the clay, as increased by the salt, is obtainable.

The agglomerate particle sizes are such that the agglomerated particles are readily pourable from a detergent box or a suitable bottle, and are not dusty. The sizes are also such that the agglomerates will disintegrate readily in aqueous media, but will not be size reduced during normal shipping and handling. The agglomerates are preferably of particle sizes like those of the spray dried detergent composition with which they are mixed to constitute the fabric softening detergent product.

The sizes of the agglomerates which satisfy these conditions are those within the No's. 10 to 140 sieve range, U.S. Sieve Series, and preferably the range is within the sieve No's. 30 to 100 (which have openings 590 to 149 microns across). Desirably, bulk densities will also be about the same, but the same bulk densities are not required, and those in the 0.2 to 0.9 g/cc range are found to result in satisfactorily non-segregating detergent compositions when mixed with

spray dried beads of 0.3 to 0.6 g/cc bulk density when the particle sizes are about the same.

To make the improved fabric softening agglomerates for use in the present invention a
5 mixture of clay and salt powders is agglomerated by being tumbled in an agglomerating apparatus, such as an inclined drum, which may be equipped with a number of breaker bars, so that the particles are in continuous movement and form a falling "screen" onto
10 which a spray of water may be directed. The finely powdered particles are preferably of a normal particle size distribution before agglomeration and the agglomerates are similarly usually of such normal distribution within their size ranges. After
15 agglomeration (and sometimes after screening, too) the particles will be of sizes in the No's. 10 to 140 sieve range (U.S. Sieve Series), although occasionally some particles as large as No's 6 and 8 Sieve (which have openings 3360 and 2380 microns
20 across, respectively) may be present. A preferred size range for the agglomerates is 10 to 100 Sieve, more preferably 30 to 100 Sieve. Still more preferably ranges are 40-100 Sieve (which have openings 420 to 149 microns across) and 40-80 Sieve
25 (which have openings 420 to 177 microns across).

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 accompanying Examples and drawings,
30 in which:-

Figure 1 is a schematic central longitudinal sectional elevational view of a rotary drum type mixer, with other equipment utilised in the practice of the process of the present invention, and

5. Figure 2 is a transverse sectional view of the said rotary drum along the plane 2-2 of Figure 1, showing the spraying of water onto the tumbling particles of clay and salt.

- Figure 1 shows an open ended, inclined,
10. cylindrical rotary drum 11 shown rotating about an axis which is at a relatively small acute angle to the horizontal, with such rotation being in the direction shown by the arrows 13 and 15. The drum 11 rests on rollers 17, 19 and 21, which rotate in the
15. opposite direction from the drum (counterclockwise, rather than clockwise, viewed from the left), causing it to turn as indicated. The rotary drum 11 contains a mixture 23 of clay and salt powders which is agglomerated in the drum into fabric softening
20. agglomerate particles due to the spraying of water onto the particles while the mixture is in motion. Final agglomerated softening particles 25 are removed from the drum 11 via a chute 27 and are subsequently dried to the desired final moisture content (including
25. removable hydrate moisture) in a suitable dryer, not illustrated. Spray nozzles 29, 31 and 33 are employed to produce essentially conical water sprays, represented by the numeral 35, which impinge on the moving mixture of clay and salt powders and promote
30. agglomeration thereof. In the rotating drum, the

- right hand or upstream third or similar part is a mixing zone wherein the clay and salt powders are dry mixed, the middle portion is a spraying and agglomerating zone, and the downstream third or so is one
5. wherein spraying is not effected, and in which the moistened particles and agglomerates are "finished" to relatively free flowing product, and the desired form and character of the agglomerate results, although the moisture content thereof is higher than
10. desired, so that a final drying operation will be undertaken.

- The foregoing description relates primarily to a rotary drum which is a preferred embodiment of the apparatus employed in the practice of the present
15. invention although other equivalent or substitute means may also be utilised. In addition to the rotary drum, supply means for adding the various final product constituents are provided. Thus, a supply tank 37 contains water or other spray solution
20. 39 (as distinguished from the spray 35), which is delivered to spray nozzles 29, 31 and 33 through a line 41. A hopper bin 43 contains clay powder 45 which is delivered to a hopper 47 by means of a delivery belt 49. Similarly, a hopper bin 51
25. contains salt powder 53 which is delivered to the hopper 47 by a delivery belt 55. Arrows 57 and 59 indicate the directions of such belt movement, respectively.

- In Figure 2 the mixture 23 in the drum 11 is
30. shown being carried up the left wall of the drum,

which is rotating in the direction of the arrow 13. As the mix 23 falls downwardly along the face 61 of the upper wall thereof the spray 35 of water, sprayed in conical patterns from the nozzle 29 and other

5. hidden nozzles 31 and 33, impinges on the moving mixture, moistens the surfaces of the clay and salt powder particles, and promotes agglomeration of the clay and salt. Thus, constantly renewing faces or

10. curtains of falling particles are contacted by the sprays and substantially uniform moistening and application of the water spray to the moving particles are obtained, which lead to production of a more uniform and better agglomerated product.

Instead of employing the described inclined drum

15. agglomerator other commercial units may be substituted, such as the O'Brien agglomerator, with breaker bars; and various mixers adapted for agglomerating, such as twin shell or V-blenders, Day mixers, or Shugi mixers. Also, the agglomeration

20. process may be either batch or continuous, and may be automated. For various agglomeration processes the powders being agglomerated will usually be about room temperature, 10 to 30°C, but the water may be at any suitable temperature, such as 10° or 20° to 40° or

25. 50°C with ambient temperature often being preferred. Residence time in the agglomerator will normally be within the range of 10 to 40 minutes, preferably 15 to 30 minutes, but it depends on agglomerator characteristics, rates of feed and speeds of rotation

30. of the drum (normally 3 to 40 rpm). Usually the

agglomeration will be halted when the desired agglomerate size distribution is reached.

After particles of agglomerate are of sizes larger than No. 100 sieve and after the overspraying
5 onto the moving surfaces of the particles of from 10 to 25% or 15 to 20% of the weight of such particles of water, so that the moisture content of the particles is raised to 15 to 35%, preferably 22 to 28% and more preferably about 25%, the moist agglomerated
10 particles are removed from the agglomerator and are dried, preferably in a fluidized bed dryer to a moisture content in the range of 5 to 16%, preferably 5 to 12% and more preferably 6 to 10% and, if the mixture of agglomerates contains particles outside
15 the 10 to 140 sieve range the agglomerates are screened or otherwise classified to be within such range, preferably within the 30 to 100 sieve range.

The agglomerate particles produced may be of any suitable bulk density, which will, to some extent,
20 depend on particle size distribution, but usually their bulk density will be within the range of 0.2 to 0.9 g/cc, more preferably 0.3 to 0.6 g/cc. Even when the fabric softener agglomerate particles are of a bulk density in the 0.5 to 0.9 g/cc range they may be
25 blended with spray dried built synthetic organic detergent beads of similar sizes, and bulk densities of 0.3 to 0.6 g/cc, and will not objectionably separate from them or segregate on storage, transportation and handling. Thus, when mixed with
30 such detergent composition particles to form fabric

softening detergent, the composition that results and is dispensed from a box of detergent will be of constant analysis and the desired softening will be obtained when the box is first opened and when it is almost finished.

The components of the preferred spray dried unitary built synthetic organic detergent beads include a synthetic organic anionic detergent, or a mixture of such detergents, a builder or a mixture of builders, and moisture, although in many instances various adjuvants may also be present. In some cases a filler, such as sodium sulphate or sodium chloride,

or a mixture thereof, may be present in the spray dried beads, too.

- 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 higher alkyl ethoxamer sulphates will similarly be of 10 or 12 to 18 carbon atoms, e.g. 12, and are also employed as the sodium salts. The higher alkyl ethoxamer sulphates will similarly be of 10 or 12 to 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 mole, preferably 3 or 5 to 20. Again, 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 sulphate is at the end thereof. Other useful anionic detergents of this sulphonate and sulphate group include the higher olefin sulphonates and paraffin sulphonates, 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 sodium linear dodecylbenzene sulphonate, sodium tridecylbenzene sulphonate, sodium tallow alcohol polyethoxy (3 EtO) sulphate, and

- sodium hydrogenated tallow alcohol sulphate. In addition to the preferred anionic 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 thereof 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 1958 by Interscience Publishers, Inc.

- Small proportions of fatty acid soaps, e.g. sodium soaps of fatty acid of 10 to 22 carbon atoms, preferably 14 to 18 carbon atoms, e.g. sodium hydrogenated tallow fatty acid soaps, can be employed, in the crutcher or post-added, as foam controllers, when less foam in the washing machine is desirable.

- Although anionic detergents are preferred, various nonionic detergents of satisfactory physical characteristics may be utilised in place of or with anionic detergents, 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. However, it is highly preferred that if it is used the nonionic detergent be a condensation product of ethylene oxide and higher fatty alcohol. In such products the higher fatty alcohol is of 10 to 20 carbon atoms, preferably

- 12 to 16 carbon atoms, and the nonionic detergent contains from about 3 to 20 or 30 ethylene oxide groups per mol, preferably from 6 to 12. Most preferably, the nonionic detergent will be one in
5. which the higher fatty alcohol is of about 12 to 13 or 15 carbon atoms and which contains from 6 to 7 or 11 moles of ethylene oxide. Such detergents are made by Shell Chemical Company and are available under the trade name Neodol (Registered Trade Marks) 23-6.5 and
10. 25-7. Among their especially attractive properties, in addition to good detergency with respect to oily stains on goods to be washed, is a comparatively low melting point, which is still appreciably above room temperature, so that they may be sprayed onto spray
15. dried base beads as a liquid which solidifies.

- The water soluble builder 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
20. mixtures thereof. Among the inorganic builders those of preference are the various phosphates, preferably polyphosphates, e.g. tripolyphosphates, such as sodium tripolyphosphate. Of course, carbonates, such as sodium carbonate, and silicates, such as sodium
25. silicate, are also useful builders and may desirably be used separately, in mixture or in conjunction with bicarbonates, such as sodium bicarbonate. Other water soluble builders that are considered to be useful supplements include the various other inorganic and
30. organic phosphates, borates, e.g. borax, citrates,

gluconates, NTA and iminodiacetates. Preferably the various builders will be in the forms of their alkali metal salts, either the sodium or potassium salts or a mixture thereof, but the sodium salts are normally highly preferred. In some instances water insoluble builders, such as zeolites, may also be present, e.g. Zeolite 4A.

When the clay-salt agglomerate particles are mixed with spray dried detergent beads, which are preferably spray dried built synthetic anionic organic detergent beads of the described particle sizes and bulk density, conventional mixing or blending equipment, such as Day mixers, may be utilised and normally only a few minutes time is needed to satisfactorily disperse the agglomerate, which will be a minor proportion of the final composition. The final fabric softening particulate detergent composition that will be made will comprise spray dried beads comprising from 5 to 25% of synthetic organic detergent, preferably all anionic detergent, 20 to 60% of inorganic builder(s) for the detergent, 5 to 40% of water soluble inorganic filler salt, which normally improves the flowability of the composition, 4 to 18% of moisture, largely present as water of hydration of the sulphate, bentonite, builders and any filler present, and 0 to 5% of adjuvant(s), the fabric softening clay-salt agglomerate will constitute the balance of the composition, normally being from 5 to 30% thereof.

30

Such agglomerate will be of 2 to 10 or 3 to 5 parts of clay, one part of salt and 5 to 16% of moisture and will be of particle sizes in the No's. 10 to 140 sieve range. The clay and salt powders that are
5 agglomerated will have major proportions thereof that pass a No. 100 sieve (less than No. 100 sieve size). In preferred embodiments of the fabric softening detergent compositions the synthetic anionic organic detergent will be a sodium linear higher alkyl
10 benzene sulphonate or mixture thereof, the inorganic builder(s) will be selected from the group consisting of sodium tripolyphosphate, sodium silicate, sodium carbonate, and mixtures thereof, the adjuvant(s) will be selected from the group consisting of sodium
15 carboxymethylcellulose, enzyme(s), colourants(s), perfume(s), optical brightener(s), and mixtures thereof, the agglomerate will be one of particle sizes in the range of No's. 30 to 100 Sieve, with major proportions of each of the finely divided clay
20 and salt components being of particle sizes less than No. 200 Sieve, with a preferred moisture content in the range of 5 to 12% and with the proportions of clay and salt being within the range of two parts of salt to 7 to 9 parts of clay. In such preferred
25 embodiments the proportion of sodium linear higher alkylbenzene sulphonate will be in the range of 10 to 20%, the proportion of inorganic builders will be in the range of 30 to 50%, the proportion of water soluble inorganic filler salt will be in the range of
30 5 to 30%, the proportion of adjuvants will be in the range

of 0.5 to 5% and the proportion of fabric softening agglomerate will be in the range of 10 to 25%. Also, the bulk densities of the product and the component agglomerate and spray dried beads may be in the 0.3 to 0.7 or 0.3 to 0.6 g/cc range. In a more preferred embodiment of the invention the synthetic anionic organic detergent will be sodium linear dodecyl benzene sulphonate, sodium linear tridecylbenzene sulphonate or mixtures thereof, the filler salt will be sodium sulphate, the builders will be sodium tripolyphosphate, sodium silicate and sodium carbonate, the agglomerate will be of a moisture content in the range of 10 to 12%, made from clay of particle sizes of about No. 325 sieve or less and salt of particle sizes such that a major proportion thereof is less than No. 200 sieve, the proportion of clay to salt in the agglomerate will be about 4:1, and the agglomerate and spray dried beads (in all cases the spray dried beads constitute the balance of the composition) will be of a bulk density of about 0.4 g/cc. In this more preferred embodiment of the fabric softening detergent composition the proportions of synthetic anionic organic detergent, sodium tripolyphosphate, sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$), sodium carbonate, sodium sulphate filler and agglomerate will be 10 to 20%, 20 to 30%, 5 to 12%, 5 to 15%, 5 to 25% and 10 to 20%, respectively.

Although the presence of sodium sulphate (anhydrous) or sodium carbonate in the agglomerate unexpectedly improves the fabric softening properties of the agglomerate so

that it is a better fabric softener than one would expect from its bentonite content, it has been found that such fabric softening effect is often reduced when certain polymeric materials (such as straight chain polyacrylates) are incorporated in the detergent compositions containing the agglomerate, such as may be done to improve detergency, soil anti-redeposition properties, processing ease, and physical characteristics of the detergent particles or beads, such as particle strength. Thus, it has been noted that when such polymers are present in the detergent compositions of the present invention, containing the agglomerate, the fabric softening action of the detergent composition is diminished objectionably. However, when the polymeric material utilised is a copolymer of maleic and acrylic acids, having a weight average molecular weight in the range of about 30,000 to 100,000, and with the proportions of maleic to acrylic moieties being in the range of 1:10 to 10:1, detergency, etc., are improved without loss of softening power. Preferably, the copolymer employed is that sold under the trade mark SOKALAN CP5, which is the sodium salt of the copolymer and which is of a weight average molecular weight in the range of about 60,000 to 70,000. Such a copolymer, when employed in the present detergent compositions at a content in the range of 0.4 to 5%, preferably 0.5 to 3%, and most preferably about 1%, improves detergency, soil anti-redeposition, processing and bead strength

without adversely affecting the softening action of the composition on laundry being hand washed.

- When the fabric softening detergent composition of the present invention is employed to wash laundry
5. it may be used in the usual manner for such products, at conventional concentrations, temperatures and washing conditions. Thus, it is useful in both hot and cold water washing, machine washing and hand washing, and the washed laundry may be dried in an
 10. automatic laundry dryer or on a wash line. In all such cases and when the agglomerate is used apart from a fabric softening detergent composition or with such, the proportion of agglomerate employed is a fabric softening proportion and when a detergent
 15. composition is present (separate or in admixture with the agglomerate) a deterative proportion is used. The detergent composition containing the agglomerate is more effective in softening washed laundry, especially cotton goods, than the same composition containing a
 20. corresponding weight of bentonite alone (without sodium sulphate), either agglomerated or not. However, most significant improvements in fabric softening effects are noted when the laundry is hand washed and line dried after rinsing. Similar results
 25. are obtainable when the component spray dried detergent beads and bentonite-sulphate agglomerate are added to wash water together or when washing is effected with the detergent composition beads, and the agglomerated bentonite-sulphate fabric softener
 30. is added to the rinse water. Still, it is much

preferred, for convenience, to employ the fabric softening detergent composition of the present invention.

- For machine washing the concentration of the
5. fabric softening bentonite-sodium sulphate agglomerate component of the fabric softening detergent composition will normally be within the range of 0.01 to 0.5% in the wash water, preferably being 0.01 to 0.03% thereof, with the balance of the
 10. composition being from 0.04 to 0.20%, preferably 0.04 to 0.12%. Preferably the percentage of fabric softening detergent composition will be 0.05 to 0.15 or 0.25%.

- When the laundry is hand washed the
15. concentration of the compositions are often much higher, sometimes being as high as 1 or 2%, with the agglomerate percentage being up to 0.1 to 0.4%. However, it is desirable for economy's sake to maintain the concentration of the fabric softening
 20. detergent composition in the 0.05 to 0.25% range, with the agglomerate being from 0.01 to 0.03 or 0.05%.

- While wash water temperatures may be varied widely, usually the water temperature will be in the range of 10 to 60°C, often being 20 to 45°C.
25. However, as in European washing practice, higher temperatures, up to about 90°C, may also be used.

- Washing times can range from 5 minutes to 45 minutes and wash water is preferably of limited hardness, normally not being in excess of 150 ppm, as
30. calcium carbonate. The automatic washing machines

employed may be of either front- or top-loading designs.

The following examples illustrate but do not limit the invention. Unless otherwise indicated, all parts are by weight and all temperatures are in °C.

EXAMPLE 1

This is concerned with the preparation of a bentonite/sodium sulphate agglomerate for use in making the compositions of the present invention.

Four parts by weight of finely divided sodium bentonite powder of particle sizes which pass through a No. 325 sieve (U.S. Sieve Series) are mixed with one part by weight of finely divided sodium sulphate (anhydrous), and the mixture is coagglomerated in an agglomerating apparatus like that illustrated in the drawings (or its equivalent), with agglomeration being effected by spraying of a finely divided water spray onto the moving surfaces of the mixing powders, while mixing is being continued. The proportion of water utilised is 22.5%, based on the final weight of the agglomerated particles removed from the rotary drum, and because the bentonite initially contains some moisture the moist agglomerated particles removed are of a moisture content of 25%. Such moisture content is that removable by heating at 105°C for five minutes, and includes hydrate and gel moisture. The throughput time for agglomeration may be varied, depending on the particular agglomerator used, the starting materials, the spray characteristics and the agglomerator speed, but will normally be about 15 to 30 minutes, which time allows for a conditioning tumbling of the moist agglomerate after the water has been sprayed onto the tumbling

- powders. The removed agglomerated particles, of particle sizes substantially all of which are in the range of 10 to 140 sieve (U.S. Sieve Series), are then dried in a fluidised bed dryer, through which
5. hot air is blown at an elevated temperature (normally from 50 to 90°C for a laboratory dryer and 250 to 550°C for a commercial or plant dryer). The use of the fluidized bed dryer, which maintains the particles in motion during drying, prevents undesired
 10. attachment of particles to each other, keeping them in essentially spherical shape, which is desirably free flowing, and promoting efficient and rapid drying, which may take as little as 5 to 20 minutes (throughput time). Drying is continued until the
 15. moisture content of the agglomerate particles is about 11%, after which any particles that are outside the range of No's. 30-100 sieve sizes are removed (usually a minor proportion). The resulting 30-100 sieve product is collected and is tested for various
 20. important end use properties. When added to water, such as wash water, the agglomerates disperse quickly, all being dispersed satisfactorily within a two minute period. This is important because particles which are slow to disperse may become
 25. entrapped in laundry and leave white smears on it, which is especially objectionable when the laundry is dark coloured. Also, slow dispersal is often accompanied by poor softening. The particles are tested for strength and are found to be satisfactory,
 30. being comparable to spray dried detergent particles

in resisting crushing and resulting powdering. When employed in a normal concentration in wash water (0.03%) with a heavy duty laundry detergent of the anionic type (sodium linear higher alkylbenzene sulphate) satisfactory softening of machine washed cotton laundry is obtained. Such softening performance is awarded a rating of 8 on a scale of 10, which is considered to be acceptable for a commercial product. When the described agglomerate is compared to agglomerated bentonite made by agglomerating the same type of bentonite powder (American Colloid Company AEG-325 mesh sodium bentonite) by means of a dilute sodium silicate solution, the softening power of the product in the test described is significantly inferior to that with the agglomerate of the present invention when the same proportions are used under the same conditions. Similarly, it has been found that one can obtain fabric softening with the present bentonite-sodium sulphate agglomerate which is equivalent to that of a measured amount of agglomerated bentonite when appreciably less (often 20% or less) of the bentonite-sulphate agglomerate is employed.

25

30

EXAMPLES 2A to 2DExample 2A

A fabric softening composition is made up having the composition given in Table 1 below.

5

TABLE 1

<u>Component</u>	<u>Percent (by weight)</u>
Sodium linear tridecylbenzene sulphonate sulphonate	17.0
10 Pentasodium tripolyphosphate	16.3
Sodium salt of copolymer of maleic and acrylic acids (SOKALAN CP5, 35% active solids, in H ₂ O [copolymer weight average molecular weight in the range of 60,000- 15 70,000], mfd. by BASF)	2.9
Sodium silicate (Na ₂ O:SiO ₂ = 1:2.4)	7.0
Sodium carbonate	5.0
Fluorescent brightener (stilbene type)	0.3
Dye (Blue Dye Mix No. 5)	0.01
20 Enzyme mixture (proteolytic and amylolytic)	0.5
Bentonite/sodium sulphate agglomerate ¹	12.0
Blue dots ²	2.0
Perfume	0.3
Sodium sulphate	32.59
25 Moisture	4.1
	<u>100.0</u>

Notes on Table 1

- 1 4:1 clay:Na₂SO₄ ratio, of particle sizes in the 10-130 sieve range, and of 11% moisture content.
- 2 Spray dried detergent composition particles or
5 similarly sized (10-100 sieve) polyphosphate beads are coloured with ultramarine blue.

A spray dried heavy duty built synthetic anionic organic detergent composition of the above formula
10 (less the bentonite/sodium sulphate agglomerate, which is made by the method described in Example 1) is made by a conventional spray drying process, and the detergent composition beads resulting are of particle sizes in the range of No's. 30 to 100 sieve, U.S.
15 Sieve Series (which have openings 590 to 149 microns across), and of a bulk density of 0.39 g/cc. The bentonite/sodium sulphate agglomerate is of a bulk density of about 0.6 g/cc, so the composition bulk density is about 0.41 g/cc. The two products are
20 blended together in a conventional mixer, such as a Day mixer, or twin-shell blender, and because they are of about the same particle size distribution, and close enough bulk densities, may be mixed together to form an essentially homogeneous particulate fabric
25 softening detergent composition containing 12% of the bentonite-sodium sulphate agglomerate particles. Such composition is non-settling during shipment, storage and use, and such non-settling characteristics therefore are verifiable by
30 shake-testing of boxes thereof and analyzing samples for different box locations.

Cotton terry towels are washed in a home laundry type washing machine at a concentration of the fabric softening detergent composition of 0.15% in city water of about 100 p.p.m. mixed calcium (30 parts) and magnesium (2 parts) hardness, as CaCO_3 , at a temperature of 25°C , using a wash cycle of about 45 minutes, including rinsing. The towels are line dried and after drying are evaluated for softness by a panel of experienced evaluators (of fabric softness). The panel found the towels to be satisfactorily soft. When an agglomerate of bentonite (no sodium sulphate) is substituted for the bentonite/sodium sulphate agglomerate

15

20

25

30

in the described composition, with the proportion of bentonite being the same in both compositions, softening results, after the described washing procedure, are noticeably inferior to the results
5 obtained when there are tested agglomerates and fabric softening detergent compositions of this example that are within the present invention.

Example 2B

When the described copolymer is omitted from the
10 formula detergency and soil anti-redeposition effects are diminished significantly and the spray dried beads resulting are not as satisfactory.

Example 2C

Also, when instead of the SOKALAN CP5 copolymer
15 there is substituted an equal proportion of straight chain polyacrylate, fabric softening of terry cloth cotton towels which are hand washed with such detergent compositions is diminished appreciably and objectionably. Thus, the present compositions,
20 containing the described copolymer, are of improved physical characteristics and washing properties and the polymer does not cause the loss of softening characteristics, as do straight chain polyacrylates.

Example 2D

25 The formula of this example may be varied by increasing the content of the SOKALAN CP5 copolymer to 7.1% (2.5% polymer on an anhydrous basis), increasing the sodium silicate content to 9.0% and adjusting the sodium sulphate and moisture contents
30 to 29.9% and 1.4%, respectively (of course the

moisture content of the product will still be 6%, as before, with 4.6% of that moisture being included in the SOKALAN CP5). Such changes in the formula improve the detergency and soil anti-redeposition, due to the increase in the copolymer, and improve anti-corrosion characteristics of the detergent composition (inhibiting corrosion of aluminium), but normally the increases in detergency and corrosion inhibition, while detectable, are not significant enough to warrant the increases in contents of SOKALAN CP5 and sodium silicate.

EXAMPLES 3A and 3B

Example 3A

A fabric softening composition is made up having the composition given in Table 2 below.

TABLE 2

<u>Component</u>	<u>Percent (by weight)</u>
Sodium linear tridecylbenzene sulphonate	20.1
Pentasodium tripolyphosphate	19.2
Sodium maleic-acrylic copolymer (SOKALAN CP5, [35% solids, in water] manufactured by BASF)	3.4
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$)	7.0
Sodium carbonate	5.9
Fluorescent brightener (stilbene type)	0.3
Dye (Blue Dye Mix No. 5)	0.01
Enzyme mixture (proteolytic and amylolytic)	0.5
Bentonite/sodium sulphate agglomerate ¹	14.0
Blue dots ²	2.0

TABLE 2 (continued)

<u>Component</u>	<u>Percent (by weight)</u>
Perfume	0.3
5 Sodium sulphate	21.99
Moisture	<u>5.3</u>
	100.0

Notes on Table 2

- 10 1 4:1 clay:Na₂SO₄ ratio, of particle sizes in the 10-130 sieve range, and of 11% moisture content.
- 2 Spray dried detergent composition particles or similarly sized polyphosphate beads coloured with ultramarine blue.
- 15 The composition of this example is essentially like that of Example 2 with the major change being in the making of spray dried detergent beads of lower bulk density (0.33 g/cc). In effect, some of the sodium sulphate had been omitted from the formula but
- 20 the consumer will be able to use the same volume of detergent per wash and obtain essentially the same cleaning power. Thus it is seen that the proportions of anionic detergent, phosphate and carbonate builder salts, copolymer and bentonite/sodium sulphate
- 25 agglomerate have all been increased so as to compensate for the lower bulk density of the product. The cost of the product has been lowered, due to the decreasing of the sodium sulphate

content. Somewhat surprisingly, the product is still non-segregating on storage and during use, despite the difference in bulk densities between the spray dried product and the bentonite/sodium sulphate agglomerate.

When tested in the same manner described in Example 2 the product of the present invention of the present example exhibits similar properties, being an excellent detergent composition and softening laundry washed with it. Also, the lighter spray dried beads are still strong enough to resist normal handling without disintegrating, and the presence of the copolymer improves processing (crutching and spray drying).

Example 3B

When the copolymer is replaced by sodium polyacrylate there is a noticeable loss in softening characteristics of the resulting detergent composition.

20

EXAMPLE 4

Results similar to those described in the previous examples are obtainable when other anionic detergents are substituted for sodium dodecylbenzene sulphonate, such as sodium linear tridecylbenzene sulphonate and mixtures thereof with sodium lauryl sulphate, and other anionic detergents of the types previously described in the specification, when other builders (previously described) are used, when other bentonites are employed and when minor adjuvants, such as colourants, are included with the bentonite

30

and sodium sulphate to be agglomerated. Also, the proportions given in the various examples that are within the invention may be varied $\pm 10\%$ and $\pm 25\%$, while remaining within the ranges specified, and the results obtained will be satisfactory, like those described.

The invention has been described with respect to bentonite, as the fabric softening smectite clay, and sodium sulphate, both of which are components of the fabric softening agglomerate according to the present invention. However, it is considered that in addition to or at least in partial replacement of bentonite other smectite clays with textile softening properties may be employed, and other finely divided water soluble ionizable salt may be substituted, at least in part, for sodium sulphate, with improved softening being obtainable compared to similar compositions from which such salt component has been omitted from the agglomerate. Still, while fabric softening smectite clays other than bentonite and water soluble salts other than sodium sulphate may also be useful, it is considered that the described bentonite-sodium sulphate agglomerates are superior to such other compositions in fabric softening properties, and are exceptional in this respect. Nevertheless, other salts than sodium sulphate may be agglomerated with the bentonite (soda ash is much preferred, of these) and favourable results may be obtained. The soda ash may be substituted for the sodium sulphate of the agglomerates of the other working examples too. It has been found that when

soda ash is substituted in whole or in part for the sodium sulphate in the agglomerate the fabric softening action of the bentonite is also increased. Of course, the soda ash should also be finely divided to be most effective. Additionally, the soda ash acts to stabilise foam and has a buffering effect, which characteristics are advantageous for hand-washing detergent compositions. Having the soda ash in the agglomerate also prevents the caking of detergent compositions, that had been noticed when the soda ash was incorporated in the crutcher mix and was an integral part of the spray dried beads. Of course, the buffering and foam stabilization effects are not pronounced when the soda ash is the sole salt in the agglomerate with the bentonite.

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

25

30

CLAIMS

1. A fabric softening particulate detergent composition which comprises from 5 to 25% of
5 synthetic anionic organic detergent, 20 to 60% of inorganic builder(s) for the detergent, 5 to 40% of water soluble inorganic filler salt, 4 to 18% of moisture, 0 to 5% of adjuvant(s), in spray dried bead
10 form, a detergency improving proportion of a water soluble copolymer of maleic and acrylic acids, optionally as a salt thereof, and 5 to 30% of fabric softening agglomerate of fabric softening clay and water soluble ionisable salt (other than silicate),
15 which agglomerate comprises particles of sizes in the range of Nos. 10 to 140 sieves, U.S. Sieve Series, (which have openings 2000 to 105 microns across), which are agglomerates of mixtures of finely divided fabric softening clay and water soluble ionisable
20 salt (other than silicate) with at least 50% by weight of each of the particles being less than No. 100 sieve size (which has openings 149 microns across), with the proportions of fabric softening clay and water soluble ionisable salt (other than silicate) being within the range of one part of salt
25 by weight to 2 to 10 parts of clay by weight, with the clay and salt particles being held together in the agglomerate particles by hydrated clay at the surfaces of the said particles, and with the agglomerate particles being of a moisture content in
30 the range of 5 to 16%, by weight.



2. A fabric softening composition as claimed in Claim 1 in which the clay is bentonite and the salt is sodium sulphate or sodium carbonate or a mixture thereof.
- 5.
3. A detergent composition as claimed in Claim 1 or Claim 2 in which the synthetic anionic organic detergent is sodium linear higher alkylbenzene sulphonate and the proportion thereof is in the range of 10 to 20%.
- 10.
4. A detergent composition as claimed in any one of Claims 1 to 3 in which the detergent is sodium linear dodecylbenzene sulphonate, sodium linear tridecylbenzene sulphonate or a mixture thereof.
- 15.
5. A detergent composition as claimed in any one of Claims 1 to 4 in which the proportion of inorganic builder(s) is in the range of 30 to 50%, the said builder(s) is/are selected from the group consisting of sodium tripolyphosphate, sodium silicate, sodium carbonate and mixtures thereof.
- 20.
6. A detergent composition as claimed in Claim 5 in which the proportions of inorganic builders are 20 to 30% of sodium tripolyphosphate, 5 to 12% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.4, and 5 to 15% of sodium carbonate.
- 25.

30.



* C L M S *

7. A detergent composition as claimed in any one of Claims 1 to 6 in which the water soluble copolymer of maleic and acrylic acids is one having a weight average molecular weight in the range of about 30,000 to 100,000.

5.

8. A detergent composition as claimed in Claim 7 in which the average weight molecular weight of the copolymer is in the range of about 60,000 to 70,000.

10.

9. A detergent composition as claimed in any one of Claims 1 to 8 in which the molar proportion of maleic acid to acrylic acid in the copolymer is within the range of 1:10 to 10:1.

15.

10. A detergent composition as claimed in any one of Claims 1 to 9 in which the copolymer is a sodium salt.

20.

11. A detergent composition as claimed in any one of Claims 1 to 10 in which the copolymer is present in an amount of 0.4 to 5% by weight.

25.

12. A detergent composition as claimed in Claim 11 in which the copolymer is present in an amount of 0.5 to 3% by weight.

30.

13. A detergent composition as claimed in Claim 11 or Claim 12 in which the copolymer is present in an amount of about 1% by weight of the composition.



* C L M S *

14. A detergent composition as claimed in Claim 1 in which the synthetic anionic organic detergent is sodium linear higher alkylbenzene sulphonate and the proportion thereof is in the range of 10 to 20%, the water soluble copolymer of maleic and acrylic acids is one having a weight average molecular weight in the range of about 30,000 to 100,000 and the proportion thereof present is in the range of 0.4 to 5%, the proportion of inorganic builder(s) is in the range of 30 to 50%, the said builder(s) is/are selected from the group consisting of sodium tripolyphosphate, sodium silicate, sodium carbonate and mixtures thereof, the proportion of water soluble inorganic filler salt is in the range of 5 to 30%, the proportion of adjuvant(s) is in the range of 0.5 to 5%, the adjuvant(s) is/are selected from the group consisting of sodium carboxymethyl cellulose, enzyme(s), colourant(s), perfume and optical brightener(s), and mixtures thereof, the proportion of fabric softening agglomerate is in the range of 10 to 25%, the agglomerate is one wherein the proportions of finely divided fabric softening clay and water soluble ionizable salt (other than silicate) are within the range of one part of water soluble ionizable salt (other than silicate) by weight to 3 to 5 parts of finely divided fabric softening clay by weight, and the spray dried beads and the agglomerates are each of a bulk density in the range of 0.3 to 0.6 g/cc.



* C L M S *

15. A detergent composition as claimed in 14 wherein the proportion of copolymer present is from 0.5 to 3%, the copolymer is a sodium salt and the molar proportion of maleic to acrylic moieties in the copolymer is in the range of 1:10 to 10:1.

16. A detergent composition as claimed in Claim 14 or Claim 15 wherein the proportion of synthetic anionic organic detergent is in the range of 10 to 20%, the detergent is sodium linear dodecylbenzene sulphate, sodium linear tridecylbenzene sulphate or a mixture thereof, the copolymer is a sodium salt of a copolymer of maleic acid and acrylic acids, with the molar proportion of maleic acid to acrylic acid being within the range of 1:10 to 10:1, and with the average weight molecular weight of the copolymer being in the range of about 60,000 to 70,000, the copolymer is about 1% of the composition, the proportions of inorganic builders are 20 to 30% of sodium tripolyphosphate, 5 to 12% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.4, and 5 to 15% of sodium carbonate, the water soluble inorganic filler salt is sodium sulphate, the proportion thereof is about 5 to 25%, the agglomerate is of finely divided bentonite which is of particle sizes of about No. 325 sieve or less, the proportion of bentonite to sodium sulphate and/or sodium carbonate in the agglomerate is about 4 to 1, and the agglomerate particles are of a moisture content in the range of 6 to 10%, the proportion of agglomerate is 10 to 20%, and the



composite fabric softening detergent composition is of a bulk density of about 0.4 g/cc.

5 17. A detergent composition as claimed in any one of Claims 1 to 16 in which the copolymer is in the spray dried portion of the composition.

10 18. A detergent composition as claimed in any one of Claims 1 to 17 in which the water soluble inorganic ionisable salt of the agglomerate is sodium sulphate.

15 19. A detergent composition as claimed in any one of Claims 1 to 17 in which the water soluble inorganic ionisable salt of the agglomerate is sodium carbonate.

20 20. A detergent composition as claimed in Claim 1 substantially as specifically described herein with reference to any one of Examples 2A, 2B, 2C, 3A and 4.

25 21. A method of simultaneously washing and softening laundry fabrics which comprises washing laundry in wash water containing a washing concentration of a detergent composition as claimed in any one of Claims 1 to 20 rinsing the laundry and drying it.

30 22. A method as claimed in Claim 21 in which the laundry is hand washed in water at a temperature in the range of 20 to 45°C and is line dried.



23. A method of simultaneously washing and softening laundry fabrics in which the wash water is at a temperature in the range of 20 to 45°C and contains 0.05 to 0.25% of a detergent composition as claimed in any one of Claims 1 to 20, the washing is machine washing, and the drying is by line drying.

10

15

20

25

30



* C L M S *