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**None**

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(54) **Fabric softening built detergent composition**

(57) A fabric softening built detergent composition, which may be in the form of a stable and pourable liquid, includes a deterative proportion of a synthetic organic detergent, a building proportion of polyacetal carboxylate builder for the detergent(s) and a fabric softening proportion of bentonite. The presence of the polyacetal carboxylate builder in the described compositions enhances the fabric softening action of the bentonite during washing of laundry.

Methods of simultaneously washing and softening fabric materials comprise washing them in wash waters containing the compositions, and then rinsing and drying. An antistatic agent, such as dimethyl distearyl ammonium chloride, may be present in a fabric softening composition and in the wash water to inhibit the development of electrostatic charges on the washed material.

**GB 2 159 533 A**

## SPECIFICATION

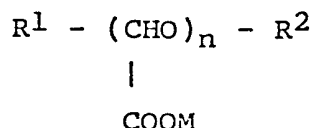
**Fabric softening built detergent composition**

- 5 This invention relates to fabric softening built detergent compositions and to processes for washing and 5  
simultaneously softening fabric materials. More particularly, it relates to such compositions which com-  
prise a synthetic organic detergent, a polyacetal carboxylate builder for such detergent and a fabric soft-  
ening proportion of bentonite, and to washing processes in which the components of such composition  
are present in the wash water.
- 10 The use of synthetic organic detergents in detergent compositions is well known, as is the employment 10  
of builders for such detergents which help to improve the deterative function thereof and to make them  
more suitable for washing heavily soiled materials. In the comparatively recent past polyacetal carboxy-  
lates have been synthesized and it has been recommended that they be employed as builders in non-  
phosphate detergent compositions because of their exceptionally good building capacities and their envi-  
15 ronmental acceptability. Such builders do not contain phosphorus and they are hydrolyzable in acidic 15  
waste water solutions, so that they are decomposed therein, whereas they are satisfactorily stable and  
effective in the normal alkaline aqueous solutions employed for washing laundry. Bentonite is known to  
possess fabric softening properties and has been suggested for incorporation in detergent compositions  
so that the fabrics washed with such compositions will have a softer feel or hand than those washed  
20 with built detergent compositions that do not contain bentonite or other suitable fabric softener. 20
- Although the various principal components of the present compositions (which components are also  
employed in the invented processes) had been suggested as constituents of detergent compositions and  
for use in washing processes, the present products and methods are novel, and possess characteristics  
that are highly beneficial and were not taught or suggested by the prior art. Thus, the combination of  
25 bentonite and polyacetal carboxylate builder with synthetic detergent results in a softening effect which 25  
is greater than that obtained with the synthetic detergent and bentonite alone, and the art does not indi-  
cate that the polyacetal carboxylate builders would have such an effect. Furthermore, when liquid deter-  
gents are made the bentonite helps to stabilize them by helping to maintain suspended the polyacetal  
carboxylate particles dispersed in the liquid medium, and at the same time the detergent, suspended  
30 particles and bentonite do not react objectionably in liquid media, as other fabric softening compounds, 30  
detergent and polyacetal carboxylate could react. Thus, the combination of components in the present  
compositions leads to significantly improved products which are novel and unobvious from the prior art.
- In accordance with the present invention a fabric softening built detergent composition comprises a  
deterative proportion of a synthetic organic detergent or a mixture of such detergents, a building propor-  
35 tion of a polyacetal carboxylate builder for such detergent(s) and a fabric softening proportion of benton- 35  
ite. Preferably such a detergent composition is a liquid detergent which comprises from 10 to 25% of an  
alkali metal metal anionic detergent salt which is a sulphated and/or sulphonated detergent having a  
higher linear alkyl or higher linear acyl lipophilic moiety, from 0 to 5% of a nonionic detergent which is a  
condensation product of a higher fatty alcohol of from 10 to 18 carbon atoms and from 3 to 20 ethylene  
40 oxide groups, from 15 to 35% of an alkali metal polyacetal carboxylate which is linear, includes from 40  
about 30 to 120 polyacetal carboxylate units in the chain thereof and is of a calculated weight average  
molecular weight in the range of from about 3,000 to 20,000, from 5 to 20% of bentonite which is of a  
swelling capacity of at least 6 ml/g and from 30 to 70% of a liquid solvent and/or dispersing medium. The  
calculated weight average molecular weight may be obtained by proton magnetic resonance (PMR)  
45 measurements, as in U.S. Patent No. 4,144,226 or by light scattering techniques. Also within the inven- 45  
tion are processes for washing and softening laundry, utilizing the components of the described compo-  
sitions, preferably in the same proportions (except for the solvent and/or dispersing medium).  
Additionally, especially in the solid or particulate solid compositions, a cationic antistatic agent (or antistat)  
50 may be present and such may be utilized in the invented processes to diminish static cling of 50  
washed and dried laundry.
- The detergents which may be employed in accordance with the present invention include anionic and/  
or nonionic detergents, with the nonionic detergent content being limited in liquid preparations to 5% of  
such compositions. The invented compositions may contain amphoteric detergents, such as the Miranols  
(Trade Mark), but the content of these will normally be limited to 5% or less of the detergent composi-  
55 tion. Similarly, cationic detergents may be present in particulate or solid compositions and sometimes 55  
may be compatible with the other components of liquid preparations but often the presence thereof will  
be avoided in liquid preparations because of possible objectionable reactions with anionic components  
thereof, such as synthetic anionic organic detergents. Some antistatic agents or antistats, which will be  
discussed later, also have deterative properties and so might be considered to be cationic detergents, but  
60 in this specification they will be referred to as antistatic agents or antistats, to identify their main function 60  
when they are present in the instant compositions and processes.

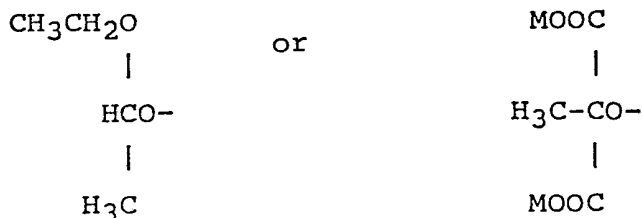
Of the anionic detergents the sulphated and/or sulphonated lipophilic materials having an alkyl chain of from 8 to 20 carbon atoms, preferably from 10 to 18 and more preferably from 12 to 16 carbon atoms, will usually be those of choice. While various water soluble salt-forming cations may be used to form the desired soluble sulphated and sulphonated detergents, including ammonium and lower alkanolamine (such as triethanolamine), and magnesium, usually an alkali metal, such as sodium or potassium, is employed, and very preferably such cation will be sodium. Among the various anionic detergents that are useful in the practice of this invention are the linear higher alkylbenzene sulphonates, the monoglyceride sulphates, higher fatty alcohol sulphates, sulphated polyethoxylated higher fatty alcohols, paraffin sulphates and olefin sulphonates, but others of this well known class may also be employed, either solely or as part of the detergent. In all of such compounds the alkyl (or acyl, for the mono-glyceride sulphates) group present will be in the range of from 10 or 12 to 18 carbon atoms. While some such alkyl groups may include branching they will still be of a carbon chain length within the described range. Although the mentioned anionic detergents are useful in the practice of the invention those which are considered as most useful and most effective, in combination with the polyacetal carboxylate builder and bentonite, are the sodium linear higher alkylbenzene sulphonates of from 10 to 18 carbon atoms in the linear alkyl moiety, preferably from 12 to 16 carbon atoms and more preferably from 12 to 14 carbon atoms, e.g. sodium linear dodecylbenzene sulphonate and sodium linear tridecylbenzene sulphonate. Also suitable anionic detergents are the sulphated polyethoxylated higher alkanols, preferably as the sodium salts, wherein such alkanols, wherein such alkanols may be synthetic or natural, and which contain from 3 to 20 or 30 ethoxy groups per mole, with the higher fatty alcohol being of from 12 to 18 carbon atoms, preferably averaging from 12 to 15 carbon atoms or 12 or 13 carbon atoms, and with the ethoxy content being from 3 to 12, preferably from 3 to 7, e.g. 3 or 5 molar proportions of ethoxy groups per mole.

The nonionic detergents, which may be employed as the primary detergents in place of the anionic detergents, especially for solid and particulate solid detergent compositions, or may be used with the anionics in the present compositions, are normally employed to only a minor extent in liquid preparations, in which the proportion thereof usually will be limited to about 5% of the composition. The nonionic detergents are preferably normally solid materials (especially when being incorporated in solid or particulate solid products) and will preferably be condensation products of ethylene oxide and a lipophile donor compound, such as higher fatty alcohols, with such a group, preferably such higher fatty alcohol, usually being of from 10 to 18 carbon atoms, preferably averaging from 12 to 15 carbon atoms, e.g. 12 or 13 carbon atoms, and with the ethylene oxide content being within the range of from 3 to 20 moles, preferably from 3 to 12 moles and more preferably from 5 to 9 moles of ethylene oxide per mole of fatty alcohol, e.g. about 6.5 or 7 moles. Among other nonionic detergents that are also useful are the ethylene oxide condensation products of alkyl phenols of from 5 to 12 carbon atoms in the alkyl groups, such as nonylphenol, in which the ethylene oxide content is from 3 to 30 moles per mole. Additionally, condensation products of ethylene oxide and propylene oxide, such as those sold under the trademark Pluronic, may be employed, as may be various others of the well known group of nonionic detergents in which a lipophilic group, such as higher alkyl (e.g. C<sub>10</sub>-C<sub>18</sub>), alkylphenyl (e.g. C<sub>7</sub> to C<sub>16</sub> alkylphenyl) or polyoxy-lower alkyl e.g. polyoxy (C<sub>1</sub>-C<sub>4</sub>) alkylene, e.g. polyoxypropylene, is joined to a polyoxyethylene ethanol by reaction with ethylene oxide.

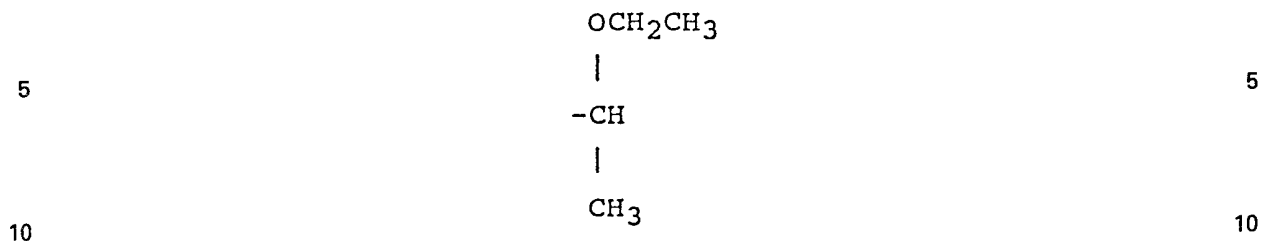
The polyacetal carboxylate may be considered to be of the type that is described in U.S. Patent 4,144,226 and may be made by the method mentioned therein. A typical such product will be of the formula



wherein M represents an alkali metal ion, an ammonium ion, an alkyl group of from 1 to 4 carbon atoms, a tetraalkylammonium group or an alkanolamine group, both of 1 to 4 carbon atoms in their alkyl moieties, n averages at least 6, and each of R<sup>1</sup> and R<sup>2</sup> is any chemically stable group which stabilizes the polymer against rapid depolymerization in alkaline solution. Preferably the polyacetal carboxylate will be one wherein M represents an alkali metal, e.g. sodium, R<sup>1</sup> represents



or a mixture thereof, R<sup>2</sup> represents

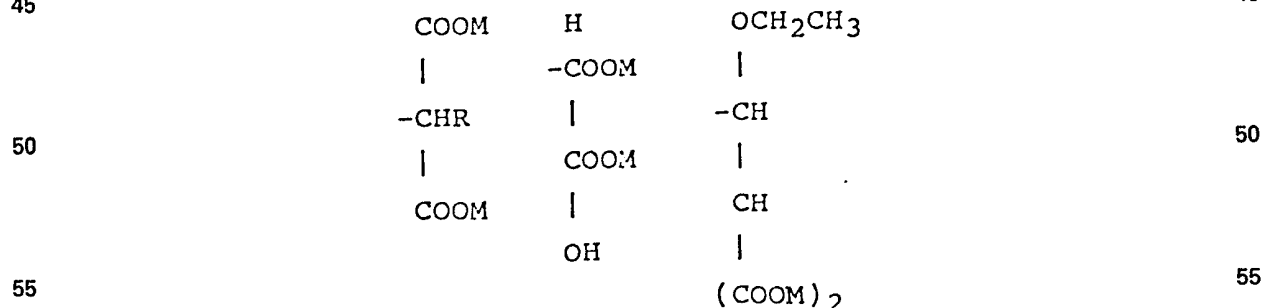


and n averages from 15 to 150, more preferably 30 to 110. The calculated weight average molecular weights of the polymers will normally be within the range of from 3,000 to 20,000, preferably from 3,000, 3,500 or 4,000 to 10,000, more preferably from 4,000 to 9,000, e.g. about 5,000 or 8,000.

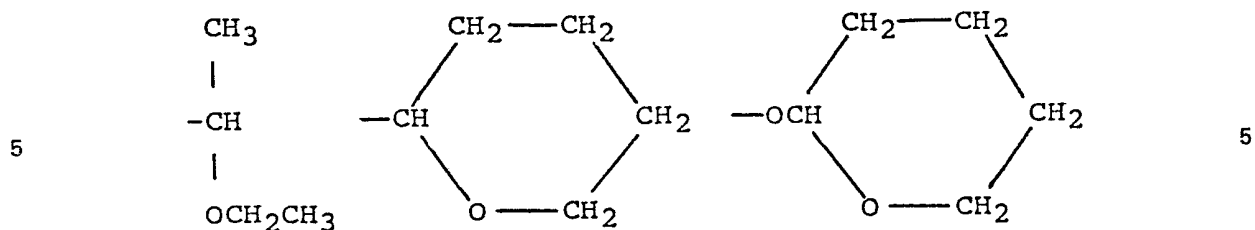
15 Although the preferred polyacetal carboxylates have been described above, it is to be understood that they may be wholly or partially replaced, at least in part, by other such polyacetal carboxylates or related organic builder salts described in various Monsanto Co. patents on such compounds, processes for the manufacture thereof and compositions, if of the same molecular weights. The various chain terminating groups described in the various patents, especially U.S. 4,144,226, may be utilized, providing that they 20 have the desired stabilizing properties, which allow the mentioned builders to be depolymerized in acidic media, facilitating biodegradation thereof in waste streams, but maintain their stability in alkaline media, such as washing solutions.

Thus, it is only necessary that the chemically reactive group stabilises the polyacetal carboxylate against rapid depolymerisation in an alkaline solution, and the specific nature of the chemically reactive 25 group is not important in the proper function of the polymer in its intended use. As an example, suitable chemically stable end groups include stable substituent moieties derived from otherwise stable compounds such as: alkanes, such as methane, ethane, propane, butane and higher alkanes such as decane, dodecane, octadecane and the like; alkenes such as ethylene, propylene, butylene, decene, dodecene and the like branched chain hydrocarbons, both saturated and unsaturated, such as 2-methyl butane, 2- 30 methyl butene, 4-butyl- 2,3-dimethyl octane and the like; aromatic hydrocarbons such as benzene, toluene, xylene and the like; cycloalkanes and cycloalkenes such as cyclohexane and cyclohexene and the like; haloalkanes such as chloromethane, chlorobutane, dichloropentane and the like; alcohols such as methanol, ethanol, 2-propanol, cyclohexanol, sodium phenate and the like; polyhydric alcohols such as 1,2-ethane diol, 1,4-benzene diol and the like; mercaptans such as methane thiol, 1,2-ethanedithiol and 35 the like; ethers such as methoxyethane methyl ether, ethyl ether, ethoxypropane and cyclic ethers such as ethylene oxide, epichlorohydrin, tetramethylene oxide and the like; aldehydes and ketones such as ethanal, acetone, propanal, methylethyl ketone and the like; and carboxylate-containing compounds such as the alkali metal salts of carboxylic acids, the esters of carboxylic acids and the anhydrides. The above listing is intended to be instructive and is not intended to be limited since chemically stable end groups 40 that stabilise the polymer against rapid depolymerisation in an alkaline solution include nitrilo groups and halides such as chlorides, bromides and the like.

Particularly suitable end groups include alkyl groups, alkyl groups containing oxygen and cyclic alkyl groups containing oxygen: such as oxyalkyl groups like methoxy, ethoxy and the like; carboxylic acids such as  $-\text{CH}_2\text{COOM}$ , 45



and the like; aldehydes, ethers and other oxygen-containing alkyl groups such as



10 and the like. In the above examples of suitable end groups, M is alkali metal, ammonium, alkanol amine, alkyl group of 1 to 4 carbon atoms and R is hydrogen or alkyl group of 1 to 8 carbon atoms. As will occur to those skilled in the art in light of the present disclosure, the chemically stable end groups at the polymer termini can be alike or unlike.

15 Other polyacetal carboxylates, which do not require specific end groups, are disclosed in U.S. Patent No. 4,315,092, which is incorporated herein by reference.

20 The bentonite employed is colloidal clay (aluminium silicate) containing montmorillonite. Montmorillonite is a hydrated aluminium silicate in which about 1/6th of the aluminium atoms may be replaced by magnesium atoms and with which varying amounts of hydrogen, sodium, potassium, calcium, magnesium and other metals may be loosely combined. The type of bentonite clay which is useful in making the invented compositions and which may be employed in the relates processes is that which has a swelling capacity of at least 3 ml/g, preferably over 6 or 7 ml/g and most preferably from about 7 to 15 ml/g. It is also preferred for such bentonite to have a cation exchange capacity greater than 30 milliequivalents per gram (meq/g), and often more than 50 meq/g. The viscosity of such a bentonite, at a 6% concentration in water, will usually be in the range of from 3 to 30 centipoises and preferably will be at least 8 centipoises. Preferred swelling bentonites of this type are the Wymong or Western bentonites, which have been sold as Thixo-jels, No's. 1, 2, 3 and 4 in the past by Georgia Kaolin Company, and which are now identified as Hi-Jells No's. 1, etc., and are sold by the same company. The words THIXO-JEL and HI-JELL are trade marks. Such materials include at least 3 or 4% of free moisture and usually contain no more than 8% thereof. They are insoluble in water and are of particle sizes substantially all of which pass through a No. 200 sieve, U.S. Sieve Series, which has openings 74 microns across and sometimes substantially all, usually 90%, 95%, 99% or more, will pass through a No. 325 sieve, which has openings 44 microns across.

35 The antistat, which is preferably incorporated in the present compositions, especially the particulate compositions, to impart to them antistatic properties so that washed and dried laundry will not cling together, is normally a cationic compound and has antistatic properties. Among these, those which are preferred as di-higher alkyl di-lower alkyl ammonium halides, wherein the higher alkyl groups are of from 10 to 18, preferably from 16 to 18 carbon atoms, the lower alkyl groups are of 1 to 3, preferably 1 carbon atom(s) and the halogens are chlorine or bromine. Among such materials there may be mentioned distearyl dimethyl ammonium chloride, di-tallow dimethyl ammonium chloride (wherein the alkyl is obtained from animal fats) and dihydrogenated tallow dimethyl ammonium bromide. However, various other such cationic materials, including N-cetyl-ethyl morpholinium ethosulphate, which also often have deodorant and germicidal properties, may also be employed. Descriptions of the various suitable anionic and cationic detergents are given in various annual publications entitled *McCutcheon's Detergents and Emulsifiers*, for example, in that issued in 1969. Also such cationics form a well known class and are described at length in the literature (as are the anionic and nonionic detergents) and therefore such do not have to be further detailed here. An acceptable apt description of such antistats is found in British Patent 1,131,092, at page 18.

45 In the compositions of the invention other builders than the polyacetal carboxylate may also be present although such are not necessary. Often it will be desired to avoid the presence of phosphorus in the detergent compositions so the polyphosphates, which have been the builders of choice in the detergent art for many years (especially pentasodium triphosphate), will preferably be omitted from the present formulations. Still, in some instances, they may be present, at least in relatively small proportions, e.g. up to 5 or 10%. Among builders other than polyphosphates such as sodium triphosphate and tetrasodium pyrophosphate, those which may be desirably incorporated in the present compositions to supplement the building action of the polyacetal carboxylate include sodium silicate, zeolites, e.g. Zeolite A, NTA, sodium citrate, sodium gluconate, borax, other borates, and other builders known in the detergent art. Fillers may be present, such as sodium sulphate and sodium chloride, to add bulk to the product when that is considered to be desirable. In the preferred liquid compositions of this invention the liquid medium is a solvent and/or dispersing medium, such as water, ethanol, isopropanol, propylene glycol and/or glycerol but other such suitable liquids may also be employed. While aqueous media are preferred in many instances, especially aqueous alcoholic media, it is within the scope of the invention to utilize non-aqueous media too. Mixtures of water and other solvents and/or dispersants may be employed, as may be mixtures of non-aqueous liquids. In the liquid compositions there may be present diluents, extenders, antifreezes and adjuvants, such as buffers, thickeners, hydrotropes and stabilizers.

Among the various other adjuvants that may be employed in particulate compositions (but some can also be used in liquids) are colourants, such as dyes and pigments, perfumes, enzymes, stabilizers, activators, (especially activators for causing active oxygen release from sodium perborate bleach, if present, in particulate or solid preparations), fluorescent brighteners, fungicides, germicides and any flow promoting agents. Also included among adjuvants, unless in other classes previously mentioned, are various additional components or impurities that may be present with other ingredients. For example, it is known that sodium carbonate and water are often present with polyacetal carboxylate in Builder U, the product which is the preferred present source of polyacetal carboxylate.

Moisture will usually be present in the solid (including particulate) compositions of the present invention, either as free moisture or in one or more hydrates. While moisture is not an essential component of these improved detergent compositions (except for the aqueous liquids) it will normally be present due to the use of water in manufacturing, and it may help to solubilize other composition components and bind them together, as is usually desired.

The proportion of total synthetic organic detergents present in the invented compositions is a deterative proportion, which may be up to 40% of the compositions but will normally be in the range of from 5 to 30 or 35%, preferably from 10 to 25% and more preferably from 10 to 20%, e.g. about 13, 14 or 15%. As was previously mentioned, in the liquid preparations the content of nonionic detergent will normally be limited to about 5%. In particulate detergents wherein only one type of detergent is employed the contents thereof will be the same as given for total detergents but frequently will be in the lower parts of the ranges given, such as 5 or 10 to 20%. With respect to particulate detergent compositions wherein a nonionic detergent is the principal deterative component the proportions thereof will usually be within the range of from 10 to 30% and sometimes lesser upper limits will be imposed, such as 25% or 22%, so that such products, which may be made by post-addition of normally solid nonionic detergent in liquid state, will be freely flowing. When combinations of anionic and nonionic detergents are utilized the proportions thereof will generally be within the range of ratios of from 1:5 to 5:1, often being in the range of 1:3 to 3:1. When mixtures of anionic detergents or mixtures of nonionic detergents are utilized the ratios thereof may vary widely, usually being within the range of from 1:10 to 10:1.

The polyacetal carboxylate component will usually be present in a proportion from 5 to 40%, preferably from 15 to 35% and more preferably from 17 to 25%, e.g. 20 to 21%. In liquid detergent preparations, to avoid producing a product which will not flow sufficiently quickly, as a practical matter the upper limit of polyacetal carboxylate content may be about 30% in some instances. The percentage of bentonite in compositions of the present invention will usually be in the range of from 3 to 25%, preferably being from 5 to 20% and more preferably being from 5 to 12%, e.g. about 8 or 10%. In liquid preparations the proportion of bentonite may be adjusted within the ranges given so as better to stabilize such preparations against separation out of the polyacetal carboxylate powder. In such liquid preparations both the polyacetal carboxylate and the bentonite will normally be in finely divided powder form, such as powders which will be in the size range of No's. 100 to 400 sieves (which have openings in the range of from 149 to 37 microns across), often passing through 200 or 325 mesh sieves (which have openings 74 microns or 44 microns across). Of course, for particulate preparations, it is preferred that the particle sizes of components should be like those of the desired final composition, if the particular component is separately incorporated in the composition, although more finely divided powders are also useful, as has been indicated. The ratio of the proportion of synthetic organic detergent to polyacetal carboxylate will normally be within the range of from 1:4 to 2:1, preferably being in the range of from 1:2 to 1:1, and the ratio of bentonite to polyacetal carboxylate will normally be in the range of from 1:5 to 1:1, preferably from 1:3 to 2:3.

The moisture content of the solid compositions of the invention will usually be in the range of from 2 to 20%, preferably from 5 to 15%, e.g. about 10%, and the liquid content of the liquid detergents will usually be from 30 to 70%, preferably from 43 to 68%, e.g. about 53 or 58%. In many instances such percentages apply to water as the sole liquid present in the liquid compositions but often a co-solvent, such as isopropanol and/or ethanol, is/are present and in such instances the ratio of water to total co-solvent will preferably be within the range of from 1:1 to 10:1. Lesser proportions of liquid medium will be utilized for cream and paste forms of the invention, with still lower proportions being in films, briquettes, pellets, bars and cakes.

The optional cationic antistatic agent will normally be present in an antistatic proportion in the range of from 2 to 10%, preferably from 4 to 6%, e.g. about 5% and the proportions of builders other than polyacetal carboxylate, if such are present, will be in the range of from 5 to 30%, often with from 5 to 20% of sodium carbonate being present, preferably from 5 to 15% thereof, and from 3 to 15% of sodium silicate being in the formula, preferably from 5 to 12%. Total adjuvants will usually not exceed 20%, preferably being 10% or less, and individual adjuvants will usually be limited to 5%, preferably 3% and more preferably about 1%, in many cases.

The manufacture of the present compositions may be conducted in any suitable conventional manner, depending on whether solid, liquid, paste or other types of products are being made. For liquid products the liquid medium, which may be a solvent, dispersant, or other functional material, or a mixture, may have the various components added to it, usually preferably with any hydrotrope being added first, followed by detergent, polyacetal carboxylate, bentonite and antistat, if present. However, admixing may be

effected simultaneously or in other sequences, too. Normally any colourants and perfumes will be added near the end of the manufacturing procedure. In some instances it may be desirable to withhold some of the solvent for final addition, whereby a final thinning of the mix may be obtained, when desired. Various types of mixers may be employed and in some instances utilization of homogenizing mixers may be preferred. Instead of the liquid form, with viscosities in the readily flowable range, normally ranging from 10 centipoises to 10,000 centipoises, such as 50 or a thousand to 10,000 cp., e.g. about 2,000 or 6,000 cp., higher viscosity liquids and non-flowable products may be produced in the same general manner, modifying the proportions of components present and changing the mixing equipment employed accordingly. The viscosity measurements given are approximate and it must be kept in mind that because the present compositions are somewhat thixotropic they can be thinned by stirring or shaking so that even if initially difficult to pour, pouring can be effected after such agitation.

To make the preferred particulate solid compositions, which will usually be of particle sizes in the 8 to 120 or 10 to 100 sieve (U.S. Sieve Series) range (having openings from 2.38 mm to 125 microns and 1.68mm to 149 microns across, respectively), it will often be preferred to spray dry as much of the formulation as is feasible, so as to obtain substantially uniformly shaped globular particles. Because the polyacetal carboxylate of the present compositions can be adversely affected by heat it may be desired to post-add it to other components of the product that have previously been spray dried to form what may be referred to as "base" beads. If the polyacetal carboxylate is to be post-added with will be preferred that it be of essentially the same shapes, particle sizes and approximate bulk density as the rest of the composition, so as to inhibit segregations during shipping and storage. However, even if more finely divided powdered polyacetal carboxylate is employed, such as that of particle sizes in the 100 or 160 to 200 or 325 mesh (or sieve number) range (having openings 149 or 193 to 44 microns across), or smaller, one finds that such particles will often adhered to the larger beads, maintain the product in the desired size range and be essentially non-segregating (although, of course, results will not be as good in this respect as when the various components of the composition are all of the same sizes, shapes and bulk density).

If the polyacetal carboxylate is spray dried with the detergent composition care will be exercised to prevent its decomposition due to its exposure to high spray tower drying air temperatures. When spray drying is unavailable or when costs are to be minimized the various components of the present compositions may be mixed together, as powders, and may be agglomerated to the desired 10 to 100 sieve size (having openings 2 mm to 149 microns across), or they may be mixed together as fine powders, usually in the 100 or 160 to 200 to 325 mesh range (having openings 149 or 193 to 74 or 44 microns across). When a nonionic detergent is to be present in the product in a significant proportion the major proportion thereof may be post-sprayed onto previously spray dried beads or onto particles of other components of the composition. Normally, no more than about 4% of nonionic detergent, on a final product basis, will be in a spray dried product, unless added after spray drying, due to decomposition of the nonionic detergent that can occur at elevated tower temperatures when more than a relatively small proportion thereof is present in the crutcher slurry being spray dried. Other temperature sensitive components of the product may also be post-added so as to avoid undesirable subjections to elevated temperatures. Thus, if a bleaching agent, such as sodium perborate, is to be present in the formulation, it will be post-added, as will be enzyme powder, antistat, perfume and other heat sensitive components, preferably as particles in the previously mentioned final desired range, or as finely divided powders of sizes previously given. Finer particles, e.g. through No's. 200 and 325 sieves (having openings 74 microns and 44 microns across respectively), may also be used. Materials like bentonite, the inorganic builders, such as sodium carbonate, sodium bicarbonate, sodium silicate and zeolites, and fillers, such as sodium sulphate, help to make strong, attractive and free flowing spray dried beads and preferably will be incorporated in crutcher slurries to be spray dried for their physical characteristics, as well for their building and filling function.

In the practice of the washing process of this invention, wherein soiled (and stained) fibrous materials, such as conventional clothing and "laundry" fabrics, of cotton, polyester-cotton blends, polyesters, acrylics, nylons, acetates, rayons and various blends thereof, are washed in an aqueous washing medium, such medium will contain a suitable detergent, as described, a polyacetal carboxylate of the desired calculated weight average molecular weight, and bentonite of the type indicated. Preferably such components will be part of a liquid or particulate solid detergent composition but it is within the invention to charge such materials separately to the wash water. The wash water may be of any suitable type, with a medium hardness water often being preferred. However, the hardness of the water may range from 0 to 400 p.p.m. or so, normally being from 50 to 200 or 300 p.p.m., with the range of 50 to 150 p.p.m. often being preferred, e.g. 100 p.p.m. The water temperature is preferably in the range of 30 to 60°C but other temperatures, as low as 5 to 10°C and as high as 70°C, and in some cases 90°C, may be employed. Washing may be by hand, with hand rinsing and line drying, or may be by automatic washing machine, which includes one or more automatic rinse cycles, followed by automatic drying. The water hardness will preferably be mixed calcium and magnesium hardness, usually being within the range of 1:1 to 10:1, e.g. 3:2 to 4:1, of calcium to magnesium.

In the wash waters the total proportions of the present compositions employed will normally be within the range of 0.05 to 0.5%, preferably 0.1 to 0.3% and more preferably about 0.15%. From the upper and lower limits of such ranges it is seen that the percentages of detergent in the wash water will normally be from 0.0025 to 0.15% preferably being 0.005 to 0.125% and more preferably being 0.01 to 0.04%.

5 When a liquid detergent is employed the percentage of nonionic detergent in the wash water will usually be in the range of 0.000 to 0.025%, in a preferred method of the invention, with anionic detergent being the balance. 5

The percentage ranges of polyacetal carboxylate and bentonite in the wash water will normally be 0.0025 to 0.2% and 0.0015 to 0.125%, preferably 0.0075 to 0.075% and 0.0025 to 0.100%, and more preferably 0.017 to 0.05% and 0.005 to 0.024%, respectively. When an antistat is present the percentage thereof 10 in the wash water will normally be from 0.002 to 0.02%, preferably 0.004 to 0.01%. The proportion of other components can be calculated from the proportions thereof previously recited for compositions of the present invention and the concentrations of such compositions recommended for use in washing. 10

Compositions and washing processes of the present invention possess significant and unexpectedly 15 beneficial advantages over the prior art softening detergent compositions and methods. The polyacetal carboxylate allows the manufacture of a satisfactory built synthetic organic detergent composition which is free of phosphorus or in which the phosphorus content can be minimized. In ecological terms the builder in such compositions is non-eutrophying and is readily biodegradable or hydrolyzable to carbon, hydrogen and oxygen compounds which are relatively innocuous. Yet, the builder is sufficiently stable to 20 be effective in washing operations. The bontonite softener is compatible with anionic synthetic organic detergents and helps to stabilize liquid compositions containing polyacetal carboxylate builder. Surprisingly the combination of anionic and/or nonionic detergent, polyacetal carboxylate builder for such detergent and bentonite fabric softener results in improved fabric softening, compared to compositions wherein the polyacetal carboxylate is replaced by the previous standard for builder excellence in the de- 25 tergent field, pentasodium tripolyphosphate. Additionally, in the liquid preparations the polyacetal carboxylate is more suspendable than sodium tripolyphosphate so the liquid detergents are more stable against undesired settling out of the builder. The various advantages cited are considered to be unexpectedly beneficial and unobvious and represent significant advances in the art. 25

The following examples illustrate the invention but do not limit it. Unless other indicated, all parts are 30 by weight and all temperatures are in °C in the examples, the specification and the claims. 30

*Examples 1A to 1Z and 1AA to 1AM*

(Examples 1C, 1F, 1P, 1S, 1AC and 1AF are comparative examples.)

35 *Example 1A* 35

	<i>Component</i>	<i>Percent</i>	
40	Sodium linear dodecylbenzene sulphonate	13	40
	Builder U (Lot 2538422, of molecular weight of 8034, 79.7% active polymer and 4.2% of sodium carbonate, with the balance being mostly water, obtainable from Monsanto Company	21	
45	Bentonite (Hi-Jell No. 1, a high swelling western bentonite of a swelling capacity in the range of 7 to 15ml/g, obtainable from Georgia Kaolin Co.)	8	45
50	Water, deionized	<u>58</u> 100	50

A liquid detergent of the above formula is made by sequentially adding to a major proportion of the water the detergent, builder and fabric softening material, and subsequently admixing the balance of the water (about 12% of the composition). Such product is then tested for its deterative and softening characteristics. It is found to be a satisfactory detergent, on a par with commercial built synthetic organic detergent compositions. With respect to softening the test employed is one wherein the wash water is of a hardness of 100 p.p.m., as calcium carbonate (3:2 Mg:Ca hardness ratio) and is at a temperature of 49°C. Two face cloths of cotton (or terrycloth) are washed in a General Electric Company automatic washing machine for ten minutes, with the wash water being of a detergent composition concentration of 0.18%, 55 followed by rinsing and drying in an automatic laundry dryer. They are then rated, by an expert in fabric softness evaluations, for softness, using a standard scale of 1 to 10, wherein 1 indicates no softness and 10 indicates excellent softness produced by the treating composition. A softness rating of 9 is awarded to the composition of this Example. 60



Essentially the same result is obtained when an equal concentration of another sodium polyacetal carboxylate (Builder U, Lot 2547312) is used (Example 1B), which has a molecular weight of 5250. However, when the experiment is repeated but the Builder U is replaced by pentasodium tripolyphosphate the softness rating is reduced to 6 (Example 1C). Such differences are readily ascertainable by the consumer and are considered to be significant.

The liquid detergent composition of Example 1A is readily pourable through a narrow necked bottle (2 cm diameter circular opening) and is stable at room temperature for at least several months, after which it has thickened somewhat but is still pourable, especially after shaking. On the contrary, the "control" composition of Example 1C, including sodium tripolyphosphate instead of Builder U, is less stable and more apt to separate, with the phosphate falling to the bottom of the container.

To raise the softening power of the polyphosphate control composition to the level to the experimental composition it will be required to increase the bentonite content (Example 1D) to approximately twice its concentration in the experimental formula (Example 1A), which, as a practical matter, is unacceptable, and in some cases could lead to production of a detergent composition which would not have the cleaning properties or the physical characteristics desired, and which would also be more expensive to manufacture.

When the various components of the experimental and control formulas of Examples 1A and 1C are increased 20% (Examples 1E and 1F), replacing equal weights of water, pourable liquid detergent compositions result which also exhibit the improved softening for the experimental formula (Example 1E) over the control (Example 1F). Such favourable results are also obtained when the concentrations of the compositions are in the 0.1 to 0.3% range in the wash water, e.g. 0.1% (Example 1G), 0.15% (Example 1H) and 0.25% (Example 1I), at hardnesses of 50 ppm (Example 1J) and 200 ppm (Example 1K) and at 20°C (Example 1L) and 35°C (Example 1M).

#### 25 *Examples 1N to 1Z*

When the Examples 1A to 1M are repeated with the individual components being added to the wash water, except for the deionized water, essentially the same results are obtained.

#### *Examples 1AA to 1AM*

30 Also, when the anionic detergent content of Examples 1A to 1M is reduced to 10%, and 3% of Neodol 23-6.5 or other nonionic detergent is added the same type of fabric softening difference results.

#### *Examples 2A to 2M and 2AA to 2AM*

The procedures of Examples 1A to 1M and 1AA to 1AM are repeated, utilizing mixtures of the three essential components of the invention in the proportions indicated, with sodium sulphate (anhydrous) replacing the deionized water. The product resulting, a powder, is of particle sizes of about 160 to 200 mesh (having diameters of from 193 to 74 microns). When subjected to washing and softening test procedures like those of the Example 1 series the detergent compositions of the present invention and the controls are both acceptable with respect to detergency but the detergent compositions in accordance with the present invention are noticeably better in softening the face cloths. Similar results are also obtainable when instead of cotton or cotton-polyester cloths there are employed fabrics of other compositions, including the synthetics and cotton-synthetic blends (polyesters, nylons, acrylics and acetates).

#### *Examples 3A to 3M and 3AA to 3AM*

45 When the formulae of Examples 2A to 2M and 2AA to 2AM are spray dried from aqueous crutcher mixes of 55% solids content at a temperature of 55°C to produce particles in the 10 to 100 sieve size range (having diameters of from 1.68 mm to 149 microns) the same testing yields essentially the same results.

#### 50 *Examples 4A to 4M and 4AA to 4AM*

When 30% (composition basis) of the sodium sulphate of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by 10% of sodium carbonate, 10% of sodium silicate ( $\text{Na}_2\text{O SiO}_2 = 1.2.4$ ) and 10% of moisture, the same testing yields essentially the same results.

#### 55 *Examples 5A to 5M and 5AA to 5AM*

When the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is wholly replaced by sodium linear tridecylbenzene sulphonate (post-added) the same testing yields essentially the same results.

#### 60 *Examples 6A to 6M and 6AA to 6AM*

When half of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium linear tridecylbenzene sulphonate the same testing yields essentially the same results.

*Examples 7A to 7M and 7AA to 7AM*

When one third of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium linear tridecylbenzene sulphonate the same testing yields essentially the same results.

5 5

*Examples 8A to 8M and 8AA to 8AM*

When one tenth of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium linear tridecylbenzene sulphonate the same testing yields essentially the same results.

10 10

*Examples 9A to 9M and 9AA to 9AM*

When the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is wholly replaced by sodium lauryl sulphate (post-added) the same testing yields essentially the same results.

15 15

*Examples 10A to 10M and 10AA to 10AM*

When half of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium lauryl sulphate the same testing yields essentially the same results.

*Examples 11A to 11M and 11AA to 11AM*

20 20

When one third of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium lauryl sulphate the same testing yields essentially the same results.

*Examples 12A to 12M and 12AA to 12AM*

25 25

When one tenth of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium lauryl sulphate the same testing yields essentially the same results.

*Examples 13A to 13M and 13AA to 13AM*

30 30

When the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is wholly replaced by sodium cocomonoglyceride (post-added) the same testing yields essentially the same results.

*Examples 14A to 14M and 14AA to 14AM*

35 35

When half of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium cocomonoglyceride the same testing yields essentially the same results.

35 35

*Examples 15A to 15M and 15AA to 15AM*

When one third of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium cocomonoglyceride the same testing yields essentially the same results.

*Examples 16A to 16M and 16AA to 16AM*

40 40

When one tenth of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by sodium cocomonoglyceride the same testing yields essentially the same results.

*Examples 17A to 17M and 17AA to 17AM*

45 45

When the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is wholly replaced by Neodol 25.7 (post-added) the same testing yields essentially the same results.

*Examples 18A to 18M and 18AA to 18AM*

50 50

When half of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by Neodol 25.7 the same testing yields essentially the same results.

*Examples 19A to 19M and 19AA to 19AM*

When one third of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by Neodol 25.7 the same testing yields essentially the same results.

55 55

*Examples 20A to 20M and 20AA to 20AM*

When one tenth of the anionic detergent of the formulae of Examples 2A to 2M and 2AA to 2AM is replaced by Neodol 25.7 the same testing yields essentially the same results.

*Note on Examples 2A to 2M and 2AA to 2AM to 20A to 20M and 20AA to 20AM.*

60 60

When the form of the product is changed, by compaction, extrusion, agglomeration or other such process or by changing the proportion of liquid medium, so that agglomerates, cakes bars, briquettes, films or pastes are produced such products also yield the same comparative improvements in softening power when of the formulas of the present invention, compared to controls.

*Examples 21A to 21M and 21AA to 21AM*

The experiments reported in Examples 2A to 2N and 2AA to 2AM which relate to the manufacture of solid or particulate solid products, are modified by replacing the same sodium sulphate filler with di-tearyl dimethyl ammonium chloride so that the compositions contain 5% thereof. The improved fabric softening previously noted with respect to the controls is still observed and the products made are noticeably less susceptible to electrostatic charge accumulation, with the result that the washed materials, especially those of synthetic organic polymers, do not cling together. Note: Such results are also obtainable with others of the cationic antistats, and when the proportions thereof that are present are 3% and 7%.

10 *Examples 22A to 22M and 22AA to 22AM* 10

When the liquid compositions of Examples 1A to 1M and 1AA to 1AM have a portion of the water thereof (10% on a composition basis) replaced by ethanol, the products resulting exhibit the same relative improvements in softening characteristics for the experimental formulas, compared to the controls. The experimental products will also be more stable, with less settling out of the polyacetal carboxylate, compared to the polyphosphate builder.

*Examples 23A to 23M and 23AA to 23AM*

When the liquid compositions of Examples 1A to 1M and 1AA to 1AM have a portion of the water thereof (10% on a composition basis) replaced by glycerol, the products resulting exhibit the same relative improvements in softening characteristics for the experimental formulae, compared to the controls. The experimental products will also be more stable, with less settling out of the polyacetal carboxylate, compared to the polyphosphate builder.

25 *Examples 24A to 24M and 24AA to 24AM* 25

When the adjuvant sodium xylene sulphonate (3%) is incorporated in the formulae of Examples 1A to 1M and 1AA to 1AM, replacing an equal weight of water, the products resulting exhibit the same relative improvements in softening characteristics for the experimental formulae, compared to the controls. The experimental products will also be more stable, with less settling out of the polyacetal carboxylate, compared to the polyphosphate builder.

*Examples 25A to 25M and 25AA to 25AM*

When the adjuvant sodium carboxymethyl cellulose (1%) is incorporated in the formulae of Examples 1A to 1M and 1AA to 1AM, replacing an equal weight of water, the products resulting exhibit the same relative improvements in softening characteristics for the experimental formulae, compared to the controls. The experimental products will also be more stable, with less settling out of the polyacetal carboxylate, compared to the polyphosphate builder.

*Examples 26A to 26M and 26AA to 26AM*

When fluorescent brightener (1%) is incorporated in the formulae of Examples 1A to 1M and 1AA to 1AM as an adjuvant, replacing an equal weight of water, the products resulting exhibit the same relative improvements in softening characteristics for the experimental formulae, compared to the controls. The experimental products will also be more stable, with less settling out of the polyacetal carboxylate, compared to the polyphosphate builder.

*Examples 27A to 27M and 27AA to 27AM*

When perfume (0.5%) is incorporated in the formulae of Examples 1A to 1M and 1AA to 1AM as an adjuvant, replacing equal weight of water, the products resulting exhibit the same relative improvements in softening characteristics for the experimental formulae, compared to the controls. The experimental products will also be more stable, with less settling out of the polyacetal carboxylate, compared to the polyphosphate builder.

*Note*

In some instances, the liquid medium for the liquid detergent may be non-aqueous e.g. polypropylene glycol, in which case similar results are obtainable.

*Example 28*

The various proportions of components given for the formulas and wash waters of the foregoing series of Examples 1 to 27 are varied  $\pm 10\%$  and  $\pm 30\%$ , maintaining such within the ranges previously taught. Similarly, the concentrations in the wash water are varied proportionately. Results indicate that significantly better softening is obtained for the experimental formulae than for the controls, and for the liquid products the experimental compositions are of better stability.

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

## CLAIMS

1. A fabric softening built detergent composition comprising a deterative proportion of a synthetic organic detergent, or a mixture of such detergents, a building proportion of a polyacetal carboxylate builder for the detergent(s) and a fabric softening proportion of bentonite. 5
2. A detergent composition according to Claim 1 which comprises 5 to 30% of a synthetic organic anionic or nonionic detergent, or a mixture thereof.
3. A detergent composition according to Claim 1 or 2 comprising from 5 to 40% of polyacetal carboxylate of calculated weight average molecular weight in the range of from 3,000 to 20,000.
- 10 4. A detergent composition according to Claim 1, 2 or 3 comprising from 3 to 25% of bentonite. 10
5. A detergent composition according to Claim 4, wherein the fabric softening activity of the detergent composition is greater than that attributable to the bentonite.
6. A detergent composition according to any one of Claims 1 to 5, which comprises an antistatic proportion of a cationic antistatic agent.
- 15 7. A detergent composition according to any one of Claims 1 to 5, which comprises an antistatic proportion of a quaternary ammonium compound which is a cationic antistatic agent which, upon washing of fabrics of synthetic organic polymers, inhibits development of static cling during automatic laundry drying. 15
8. A detergent composition according to Claim 2 wherein the anionic detergent is a sulphated and/or 20 sulphonated detergent or a mixture thereof. 20
9. A detergent composition according to Claim 2, wherein the nonionic detergent is a higher alcohol polyethoxylate, an alkylphenol polyethoxylate or a condensation polymer of ethylene oxide and propylene oxide.
10. A detergent composition according to any one of Claims 1 to 9, wherein the polyacetal carboxylate polymer is linear and includes about 15 to 150 polyacetal carboxylate units in the chain thereof. 25
11. A detergent composition according to any one of Claims 1 to 10, wherein the bentonite is one having a swelling capacity of at least 3 ml/g.
12. A liquid detergent composition according to anyone of Claims 1 to 11 which comprises a liquid solvent and/or dispersing medium.
- 30 13. A liquid detergent composition as claimed in Claim 12, in which the anionic detergent, when present, is a sulphated and/or a sulphonated detergent having a higher linear alkyl or higher linear acyl lipophilic moiety and is an alkali metal salt. 30
14. A liquid detergent composition as claimed in Claim 12 or 13, in which the nonionic detergent, when present, is a condensation product of a higher fatty alcohol of 10 to 18 carbon atoms and 3 to 20 35 ethylene oxide groups. 35
15. A liquid detergent composition as claimed in Claim 12, 13 or 14, wherein the polyacetal carboxylate polymer is linear and includes from 30 to 120 polyacetal carboxylate units in the chain thereof and the anion of the carboxylate is alkali metal ion.
16. A liquid detergent composition as claimed in any one of Claims 12 to 15, wherein the bentonite is 40 of a swelling capacity of at least 6 ml/g. 40
17. A liquid detergent composition as claimed in any one of Claims 12 to 16, wherein the anionic detergent, when present, is present in an amount of from 10 to 25% by weight.
18. A liquid detergent composition as claimed in any one of Claims 12 to 17, wherein nonionic detergent is present in an amount of from 0 to 5% by weight.
- 45 19. A liquid detergent composition as claimed in any one of Claims 12 to 18, wherein the polyacetal carboxylate is present in an amount of from 15 to 35% by weight. 45
20. A liquid detergent composition as claimed in any one of Claims 12 to 19, wherein the bentonite is present in an amount of from 5 to 20% by weight.
21. A liquid detergent composition as claimed in any one of Claims 12 to 20, wherein the solvent and/or dispersant is/are present in an amount of from 30 to 70% by weight. 50
22. A liquid detergent composition according to any one of Claims 12 to 21 wherein the medium comprises water, ethanol, isopropanol, glycerol and/or polyethylene glycol.
23. A liquid detergent composition according to Claim 22 wherein the synthetic organic detergent is a sodium linear higher alkylbenzene sulphonate in which the alkyl group has from 10 to 18 carbon atoms.
- 55 24. A liquid detergent composition according to Claim 22 or 23, wherein the polyacetal carboxylate is of a calculated weight average molecular weight in the range of from 3,000 to 10,000 and the linear polymer has from 30 to 110 polyacetal carboxylate units in the chain. 55
25. A liquid detergent composition according to Claim 22, 23 or 24, wherein the bentonite has a swelling capacity in the range of from 7 to 15 g/ml.
- 60 26. A liquid detergent composition as claimed in Claim 23, wherein sodium linear alkylbenzene sulphonate is present in an amount of 10 to 20% by weight. 60
27. A liquid detergent composition as claimed in Claim 24, wherein the polyacetal carboxylate is present in an amount of from 17 to 25% by weight.
28. A liquid detergent composition as claimed in Claim 25, wherein the bentonite is present in an 65 amount of from 5 to 12% by weight. 65

29. A liquid detergent composition as claimed in Claim 26, wherein the liquid medium is present in an amount of from 43 to 68% by weight.
30. A liquid detergent composition according to Claim 22 wherein the synthetic organic detergent is sodium linear dodecylbenzene sulphonate.
- 5 31. A liquid detergent composition as claimed in Claim 22 or 23, wherein the polyacetal carboxylate is of a calculated weight average molecular weight of about 8,000. 5
32. A liquid detergent composition as claimed in Claim 22, 23 or 24, wherein the bentonite is a western bentonite having a cation exchange capacity greater than 50 milliequivalents per 100 grams.
33. A liquid detergent composition as claimed in any one of Claims 22 to 31, wherein the liquid medium is water. 10 10
34. A liquid detergent composition as claimed in Claim 30, wherein the detergent is present in an amount of about 14% by weight.
35. A liquid detergent composition as claimed in Claim 31, wherein the polyacetal carboxylate is present in an amount of about 20% by weight.
- 15 36. A liquid detergent composition as claimed in Claim 32, wherein the bentonite is present in an amount of about 10% by weight. 15
37. A liquid detergent composition as claimed in Claim 33, wherein the water is present in an amount of about 43% by weight, with any balance being accounted for by adjuvants.
38. A detergent composition substantially as herein described with reference to any one of Examples other than the comparative examples. 20 20
39. A method of simultaneously washing and softening fabric materials which comprises washing, in water, such materials with a detergent proportion of a synthetic organic detergent or a mixture of such detergents, a building proportion of a polyacetal carboxylate builder for the detergent(s) and a fabric softening proportion of bentonite, rinsing the materials and drying them.
- 25 40. A method according to Claim 39 wherein the washing is by hand. 25
41. A method as claimed in Claim 39 or 40, wherein the drying is line drying.
42. A method according to Claim 39, 40 or 41 wherein the wash water contains an antistatic proportion of an antistatic agent.
43. A method according to Claim 39, which comprises washing the materials in an automatic washing machine. 30 30
44. A method according to any one of Claims 39 to 43, which comprises washing the materials for a period of from 2 to 30 minutes.
45. A method according to any one of Claims 39 to 44, which comprises washing the materials in a wash water at a temperature in the range of 10 to 70°C.
- 35 46. A method according to any one of Claims 39 to 45, which comprises washing the materials in water whose hardness is in the range of 0 to 300 p.p.m., as calcium carbonate. 35
47. A method according to any one of Claims 39 to 46, wherein in the wash water, there is present from 0.0025 to 0.15% of a synthetic organic anionic and/or nonionic detergent.
48. A method according to any one of Claims 39 to 47, wherein, in the wash water, there is present 40 from 0.0025 to 0.2% of polyacetal carboxylate of calculated weight average molecular weight in the range of from 3,000 to 20,000. 40
49. A method according to any one of Claims 39 to 48, wherein, in the wash water, there is present from 0.0015 to 0.125% of bentonite, and the fabric softening activity of the wash water is greater than that attributable to the bentonite content thereof.
- 45 50. A method according to any one of Claims 39 to 45, wherein the wash water is of a hardness in the range of from 50 to 150 p.p.m., as calcium carbonate. 45
51. A method as claimed in any one of Claims 39 to 44, wherein the wash water is at a temperature in the range of from 30 to 60°C.
52. A method as claimed in any one of Claims 39 to 46, wherein the wash water includes 0.005 to 50 0.125% of anionic detergent which is a sulphated and/or sulphonated detergent having a higher linear alkyl or higher linear acyl lipophilic moiety and which is an alkali metal salt. 50
53. A method as claimed in any one of Claims 39 to 46, wherein the wash water includes 0.000 to 0.025% of a nonionic detergent which is a condensation product of a higher fatty alcohol of 10 to 18 carbon atoms and 3 to 20 ethylene oxide groups.
- 55 54. A method as claimed in any one of Claims 39 to 47, wherein the wash water includes 0.0075 to 0.175% of a linear polyacetal carboxylate polymer of from 30 to 120 polyacetal carboxylate units in the chain thereof and of a calculated weight average molecular weight in the range of from 3,000 to 10,000. 55
55. A method as claimed in any one of Claims 39 to 48, wherein the wash water includes 0.0025 to 0.100% of bentonite, which has a swelling capacity of at least 3 ml/g.
- 60 56. A method as claimed in any one of Claims 39 to 55, wherein drying of the washed materials is by automatic laundry dryer drying or line drying. 60
57. A method according to any one of Claims 39 to 46, wherein the synthetic organic detergent is sodium linear higher alkylbenzene sulphonate in which the alkyl moiety is of 12 to 14 carbon atoms.
58. A method according to any one of Claims 39 to 47, wherein the polyacetal carboxylate is of a 65 calculated weight average molecular weight in the range of from 4,000 to 9,000. 65

59. A method according to any one of Claims 39 to 48, wherein the bentonite has a swelling capacity in the range of 7 to 15 g/ml.
60. A method according to Claim 57, wherein the detergent is present in an amount of from 0.01 to 0.04%.
- 5 61. A method according to Claim 58, wherein the polyacetal carboxylate is present in an amount of from 0.017 to 0.05%. 5
62. A method according to Claim 59, wherein the bentonite is present in an amount of from 0.005 to 0.024%.
- 10 63. A method according to any one of Claims 39 to 62, wherein the wash water comprises from 0.002 to 0.02% of distearyl dimethyl ammonium chloride, as an antistat. 10
64. A method of simultaneously washing and softening fabric materials as herein described with reference to any one of the Examples other than the comparative examples.

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