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(54) **UTILISATION D'ALCOOLS POLYVINyliQUES COMME
ADJUVANTS DE DETERGENTS PERMETTANT
L'ELIMINATION DE SALISSURES**
(54) **USE OF POLYVINYL ALCOHOLS AS SOIL RELEASE
DETERGENT ADDITIVES**

(57) The cleaning performance of laundry detergents was to be improved. This was essentially achieved by using polyvinyl alcohol.



Abstract

The cleaning performance of laundry detergents was to be improved. This was essentially achieved by using polyvinyl alcohol.

USE OF POLYVINYL ALCOHOLS AS SOIL RELEASE DETERGENT ADDITIVES

Field of the Invention

This invention relates to the use of polyvinyl alcohol as a soil release polymer for boosting the cleaning performance of detergents in the washing of textiles, particularly textiles consisting of or containing cotton, and to detergents containing polyvinyl alcohol in combination with a certain
5 surfactant system.

Background of the Invention

Besides the ingredients essential to the washing process, such as surfactants and builders, detergents generally contain other constituents
10 which may be collectively referred to as washing auxiliaries and which comprise such diverse groups of active substances as foam regulators, redeposition inhibitors, bleaching agents, bleach activators and dye transfer inhibitors. Auxiliaries of the type in question also include substances which provide the fibers with soil-repellent properties and
15 which, if present during the washing process, support the soil release capacity of the other detergent ingredients. The same also applies to cleaning compositions for hard surfaces. Substances such as these are often referred to as soil release agents or, by virtue of their ability to provide the treated surface - for example the fibers - with soil-repellent properties,
20 as soil repellents. By virtue of their chemical similarity to polyester fibers, copolyesters containing dicarboxylic acid units, alkylene glycol units and polyalkylene glycol units are particularly effective soil release agents for polyester fabrics. Soil release copolyesters of the type mentioned and their use in detergents have been known for some time.

25 For example, **DE-OS 16 17 141** describes a washing process using polyethylene terephthalate/polyoxyethylene glycol copolymers. **DE-OS 22**

00 911 relates to detergents containing a nonionic surfactant and a copolymer of polyoxyethylene glycol and polyethylene terephthalate. **DE-OS 22 53 063** mentions acidic textile finishes containing a copolymer of a dibasic carboxylic acid and an alkylene or cycloalkylene polyglycol and, optionally, an alkylene or cycloalkylene glycol. Polymers of ethylene terephthalate and polyethylene oxide terephthalate, in which the polyethylene glycol units have molecular weights of 750 to 5,000 and the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate is 50:50 to 90:10, and their use in detergents are described in German patent **10 DE 28 57 292**. According to **DE-OS 33 24 258**, ethylene terephthalate/polyethylene oxide terephthalate polymers with molecular weights of 15,000 to 50,000, in which the polyethylene glycol units have molecular weights of 1,000 to 10,000 and the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate is 2:1 to 6:1, may be used in detergents. European patent **15 EP 0 066 944** relates to fabric treatment compositions containing a copolyester of ethylene glycol, polyethylene glycol, aromatic dicarboxylic acid and sulfonated aromatic dicarboxylic acid in certain molar ratios. European patent **EP 0 185 427** mentions methyl-terminated or ethyl-terminated polyesters containing ethylene and/or **20 propylene terephthalate and polyethylene oxide terephthalate units and detergents containing this soil release polymer. European patent EP 0 241 984** relates to a polyester containing substituted ethylene units and glycerol units in addition to oxyethylene groups and terephthalic acid units. European patent **EP 0 241 985** discloses soil release polyesters which, in addition to oxyethylene groups and terephthalic acid units, contain 1,2-**25 propylene, 1,2-butylene and/or 3-methoxy-1,2-propylene groups and glycerol units and which are terminated by C₁₋₄ alkyl groups. European patent EP 0 253 567** relates to soil release polymers with a molecular weight of 900 to 9,000 of ethylene terephthalate and polyethylene oxide **30 terephthalate, the polyethylene glycol units having molecular weights of**

300 to 3,000 and the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate being 0.6 to 0.95:1. Polyesters containing polypropylene terephthalate and polyoxyethylene terephthalate units which are at least partly terminated by C₁₋₄ alkyl or acyl groups are known from
5 European patent application EP 0 272 033. European patent EP 0 274 907 describes sulfoethyl-terminated terephthalate-containing soil release polyesters. According to European patent application EP 0 357 280, soil release polyesters containing terephthalate, alkylene glycol and poly-C₂₋₄-glycol units are prepared by sulfonation of unsaturated terminal groups.
10 The graft copolymers of polyalkylene oxides based on ethylene oxide, propylene oxide and/or butylene oxide and optionally partly saponified vinyl acetate known from European patent EP 0 219 048 also have a soil release effect.

The polymers known from this extensive prior art are attended by
15 the disadvantage that they have little, if any, effect in textiles which do not consist or do not predominantly consist of polyester. A large number of modern textiles consist of cotton or cotton/polyester blends so that there is a need for soil release polymers with a better effect even against fatty soils on such textiles.

20 It has surprisingly been found that this problem can be solved by using polyvinyl alcohols.

The present invention relates to the use of polyvinyl alcohol for boosting the cleaning performance of detergents in the washing of textiles, particularly when the textiles consist of or contain cotton.

25 Polyvinyl alcohols cannot be obtained by direct polymerization processes because the basic monomer required, namely vinyl alcohol, does not exist. Accordingly, polyvinyl alcohols are prepared by polymer-analog reactions, more particularly by hydrolysis and, on an industrial scale, above all by the alkali-catalyzed transesterification of polyvinyl
30 acetates with alcohols (for example methanol) in solution.

Polyvinyl alcohols preferably used in accordance with the invention, which are generally marketed as white-yellowish powders or granules, have molecular weights in the range from 3000 g/mole to 320,000 g/mole and more particularly in the range from 8000 g/mole to 200,000 g/mole (corresponding to degrees of polymerization of about 75 to 8000 and, more particularly, in the range from about 200 to 5000). They preferably have degrees of hydrolysis of 20% by weight to 100% by weight and, more particularly, in the range from 30% by weight to 90% by weight. Polyvinyl alcohols with molecular weights of 10,000 g/mole to 100,000 g/mole (corresponding to degrees of polymerization of 500 to 2500) and degrees of hydrolysis of 85% by weight to 90% by weight may also be used.

Accordingly, these polyvinyl alcohols are completely or partly saponified polyvinyl alcohol esters, more particularly polyvinyl acetates, with a residual content of acyl groups, more particularly acetyl groups, of up to about 80% by weight and, more particularly, from 10% by weight to 12% by weight. The polyvinyl alcohols may be characterized more closely by indication of the degree of polymerization of the starting polymer, the degree of hydrolysis, the saponification number or the solution viscosity. Polyvinyl alcohols have a high degree of purity and only contain at most 3% by weight of methanol.

The transition temperatures of polyvinyl alcohols are dependent upon the acetyl group content, the distribution of the acetyl groups along the chain and the tacticity of the polymers. Fully saponified polyvinyl alcohols have a glass transition temperature of 85°C, the value for partly (87-89%) saponified products being distinctly lower at around 58°C. Depending on their degree of hydrolysis, polyvinyl alcohols which normally have a density of about 1.2 to 1.3 g/cm³ are normally soluble in water and highly polar organic solvents, such as formamide, dimethyl formamide and dimethyl sulfoxide and are not attacked by (chlorinated) hydrocarbons,

esters, fats and oils. Polyvinyl alcohols are classified as toxicologically safe and are biodegradable.

If desired, other soil release polymers, more particularly polyester-active soil release polymers, may be used in addition to the polyvinyl alcohols. These other soil release polymers include copolyesters of dicarboxylic acids, for example adipic acid, phthalic acid or terephthalic acid, diols, for example ethylene glycol or propylene glycol, and polydiols, for example polyethylene glycol or polypropylene glycol. Soil release polyesters preferably used include compounds which, formally, can be obtained by esterifying two monomers, the first monomer being a dicarboxylic acid HOOC-Ph-COOH and the second monomer being a diol $\text{HO-(CHR}^{11}\text{)}_a\text{OH}$, which may also be present as polymeric diol $\text{H-(O-(CHR}^{11}\text{)}_a\text{)}_b\text{OH}$. In these formulae, Ph represents an o-, m- or p-phenylene group which may carry 1 to 4 substituents selected from C_{1-22} alkyl groups, sulfonic acid groups, carboxyl groups and mixtures thereof, R^{11} is hydrogen, a C_{1-22} alkyl group or mixtures thereof, a is a number of 2 to 6 and b is a number of 1 to 300. The polyesters obtainable from these monomers preferably contain both monomer diol units $\text{O-(CHR}^{11}\text{)}_a\text{O-}$ and polymer diol units $\text{-(O-(CHR}^{11}\text{)}_a\text{)}_b\text{O-}$. The molar ratio of monomer diol units to polymer diol units is preferably 100:1 to 1:100 and, more preferably, 10:1 to 1:10. In the polymer diol units, the degree of polymerization b is preferably in the range from 4 to 200 and more preferably in the range from 12 to 140. The molecular weight or rather the average molecular weight or the maximum of the molecular weight distribution of preferred soil release polyesters is in the range from 250 to 100,000 and more preferably in the range from 500 to 50,000. The acid on which the group Ph is based is preferably selected from terephthalic acid, isophthalic acid, phthalic acid, trimellitic acid, mellitic acid, the isomers of sulfophthalic acid, sulfoisophthalic acid and sulfoterephthalic acid and mixtures thereof. If their acid groups are not part of the ester bonds in the polymer, they are

preferably present in salt form, more particularly as alkali metal or ammonium salts. Of these, the sodium and potassium salts are particularly preferred. If desired, small amounts of the monomer HOOC-Ph-COOH , more particularly no more than 10 mole-%, based on the percentage content of Ph with the meaning defined above, may be replaced by other acids containing at least two carboxyl groups in the soil release polyester. These acids include, for example, alkylene and alkenylene dicarboxylic acids, such as malonic acid, succinic acid, fumaric acid, maleic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid. The preferred diols $\text{HO-(CHR}^{11}\text{)}_a\text{OH}$ include those in which R^{11} is hydrogen and a is a number of 2 to 6 and those in which a has a value of 2 and R^{11} is selected from hydrogen and alkyl groups containing 1 to 10 and, more particularly, 1 to 3 carbon atoms. Among the last-mentioned diols, those with the formula $\text{HO-CH}_2\text{-CHR}^{11}\text{-OH}$, where R^{11} is as defined above, are particularly preferred. Examples of diol components are ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, octane-1,8-diol, decane-1,2-diol, dodecane-1,2-diol and neopentyl glycol. Among the polymeric diols, polyethylene glycol with an average molecular weight of 1,000 to 6,000 is particularly preferred. If desired, these polyesters may also be end-capped, suitable terminal groups being alkyl groups containing 1 to 22 carbon atoms and esters of monocarboxylic acids. The terminal groups attached via ester bonds may be based on alkyl, alkenyl and aryl monocarboxylic acids containing 5 to 32 carbon atoms and, more particularly, 5 to 18 carbon atoms. These include valeric acid, caproic acid, oenanthic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, undecenoic acid, lauric acid, lauroleic acid, tridecanoic acid, myristic acid, myristoleic acid, pentadecanoic acid, palmitic acid, stearic acid, petroselic acid, petroselaidic acid, oleic acid, linoleic acid, linolaidic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, arachidonic acid,

behenic acid, erucic acid, brassidic acid, clupanodonic acid, lignoceric acid, cerotic acid, melissic acid, benzoic acid which may contain 1 to 5 substituents with a total of up to 25 carbon atoms, more particularly 1 to 12 carbon atoms, for example tert.butyl benzoic acid. The terminal groups
5 may also be based on hydroxymonocarboxylic acids containing 5 to 22 carbon atoms which include, for example, hydroxyvaleric acid, hydroxycaproic acid, ricinoleic acid, the hydrogenation product thereof, hydroxystearic acid and o-, m- and p-hydroxybenzoic acid. The hydroxymonocarboxylic acids may in turn be attached to one another by their
10 hydroxyl group and their carboxyl group and, accordingly, may occur repeatedly in one and the same terminal group. The number of hydroxymonocarboxylic acid units per terminal group, i.e. their degree of oligomerization, is preferably in the range from 1 to 50 and, more preferably, in the range from 1 to 10. A preferred embodiment of the
15 invention is characterized by the use of polymers of ethylene terephthalate and polyethylene oxide terephthalate, in which the polyethylene glycol units have molecular weights of 750 to 5,000 and the molar ratio of ethylene terephthalate to polyethylene oxide terephthalate is 50:50 to 90:10, in combination with polyvinyl alcohol. In another preferred embodiment of the
20 invention, graft copolymers of polyalkylene oxides based on ethylene oxide, propylene oxide and/or butylene oxide and optionally partly saponified vinyl acetate, in which the ratio by weight of polyalkylene oxides to vinyl acetate is 1:0.2 to 1:10, are used in combination with polyvinyl alcohol. If other soil release polymers are present, ratios by weight of
25 polyvinyl alcohol to other soil release polymer of 10:1 to 1:10 and more particularly in the range from 5:1 to 1:5 are preferred.

The use according to the invention in the context of a washing process may be carried out by separately adding the polyvinyl alcohol to a detergent-containing liquor or by introducing the polyvinyl alcohol into the
30 liquor as part of the detergent. Accordingly, the present invention also

relates to a detergent containing polyvinyl alcohol and 5% by weight to 30% by weight and, more particularly, 10% by weight to 25% by weight of surfactant, the polyvinyl alcohol content preferably being 0.1% by weight to 10% by weight and more preferably 1% by weight to 4% by weight. In
5 another preferred embodiment of detergents according to the invention and of the use according to the invention, the ratio by weight of surfactant to polyvinyl alcohol may be in the range from 20:1 to 5:1 and, more particularly, in the range from 15:1 to 7:1. The polyvinyl alcohol may be used in the form of an intimate mixture with the other detergent ingredients.
10 One preferred embodiment of the invention is characterized by the use of a detergent product which contains at least part of the polyvinyl alcohol in the form of a bag of polyvinyl alcohol or polyvinyl alcohol-containing material which holds the rest of the detergent ingredients and optionally the rest of the polyvinyl alcohol. Films or capsules of polyvinyl alcohol for packaging
15 detergent doses, more particularly detergent doses pre-portioned for one wash cycle, are known, for example, from International patent applications **WO 98/30670**, **WO 97/35955**, **WO 95/18215** and **WO 91/7202** and from German patent applications **DE 195 21 140** and **DE 44 16 481**. By introducing detergent doses thus packaged into water, in which both the
20 polyvinyl alcohol present in the packaging material and the remaining detergent dissolve or disperse, it is possible particularly easily to make use of the use of the polyvinyl alcohol according to the invention.

Solid detergents according to the invention or solid detergents packed in polyvinyl alcohol-containing material can be conventionally
25 produced by spray drying of an aqueous slurry of these constituents or may be obtained by agglomeration granulation of the more or less solid constituents. A particularly preferred production process is granulation under pressure, preferably in extruders to form endless strands which are then cut by blades to the required particle size. One such process is
30 described in detail in European patent **EP 0 486 592**. One example of the

production of granular detergents in high-speed mixers can be found in International patent application **WO 93/23523**. The detergent preferably has a bulk density of more than 500 g/l, a practical upper limit being about 1400 g/l although this may even be exceeded in individual cases. The bulk
5 density of the detergent is preferably in the range from 600 g/l to 1200 g/l and more preferably in the range from 700 g/l to 1000 g/l. The mean particle size of the detergent is preferably in the range from 0.8 mm to 6 mm, more preferably in the range from 1 mm to 3 mm and most preferably in the range from 1.2 mm to 2 mm.

10 Detergents containing a polyvinyl alcohol to be used in accordance with the invention may contain any other typical detergent ingredients which do not interact undesirably with the soil release polymer. For the purposes of the use according to the invention, polyvinyl alcohol is incorporated in detergents in quantities of preferably 0.1% by weight to 5%
15 by weight and more preferably 0.5% by weight to 2.5% by weight and develops a pronounced soil release effect in the practical application of such detergents. Since this soil release effect is less pronounced where relatively large quantities of nonionic surfactants are present, detergents according to the invention or detergents intended to be used together with
20 the polyvinyl alcohol used in accordance with the invention preferably contain no more than 60% by weight of nonionic surfactant, the nonionic surfactant being selected in particular from fatty alkyl polyglycosides, fatty alkyl polyalkoxylates, more particularly ethoxylates and/or propoxylates, fatty acid polyhydroxyamides and/or ethoxylation and/or propoxylation
25 products of fatty alkyl amines, vicinal diols, fatty acid alkyl esters and/or fatty acid amides and mixtures thereof.

Nonionic surfactants suitable for use in detergents according to the invention or in detergents in whose presence polyvinyl alcohol is used in accordance with the invention include the alkoxylates, more particularly the
30 ethoxylates and/or propoxylates, of saturated or mono- to polyunsaturated

linear or branched alcohols containing 10 to 22 carbon atoms and preferably 12 to 18 carbon atoms. The degree of alkoxylation of the alcohols is generally between 1 and 20 and preferably between 3 and 10. They may be produced in known manner by reaction of the corresponding
5 alcohols with the corresponding alkylene oxides. Fatty alcohol derivatives are particularly suitable, although branched-chain isomers thereof, more particularly so-called oxoalcohols, may also be used for the production of useful alkoxylates. Accordingly, the alkoxylates and, in particular, the ethoxylates of primary alcohols with linear radicals, more particularly
10 dodecyl, tetradecyl, hexadecyl or octadecyl radicals, and mixtures thereof are suitable. Corresponding alkoxylation products of alkylamines, vicinal diols and carboxylic acid amides, which correspond to the alcohols mentioned in regard to the alkyl moiety, may also be used. Also suitable are the ethylene oxide and/or propylene oxide insertion products of fatty
15 acid alkyl esters, which may be produced by the process described in International patent application **WO 90/13533**, and the fatty acid polyhydroxyamides obtainable by the processes according to US patents **US 1,985,424**, **US 2,016,962** and **US 2,703,798** and to International patent application **WO 92/06984**. Alkyl polyglycosides suitable for incorporation in
20 the detergents according to the invention are compounds corresponding to the general formula $(G)_n-OR$, where R is an alkyl or alkenyl group containing 8 to 22 carbon atoms, G is a glucose unit and n is a number of 1 to 10. Compounds such as these and their production are described, for example, in European patent applications **EP 0 092 355**, **EP 0 301 298**, **EP**
25 **0 357 969** and **EP 0 362 671** and in US patent **US 3,547,828**. The glycoside component $(G)_n$ is an oligomer or polymer of naturally occurring aldose or ketose monomers, including in particular glucose, mannose, fructose, galactose, talose, gulose, altrose, allose, idose, ribose, arabinose, xylose and lyxose. The oligomers consisting of these glycosidically linked
30 monomers are characterized not only by the type of sugars present in

them, but also by the number of sugars present, the so-called degree of oligomerization. As an analytically determined quantity, the degree of oligomerization n is generally a broken number with a value of 1 to 10 and, in the case of the glycosides preferably used, below 1.5 and, more particularly, between 1.2 and 1.4. By virtue of its ready availability, glucose is the preferred monomer unit. The alkyl or alkenyl moiety R of the glycosides also preferably emanates from readily available derivatives of renewable raw materials, more particularly from fatty alcohols, although branched-chain isomers thereof, particularly so-called oxoalcohols, may also be used for the production of useful glycosides. Accordingly, primary alcohols containing linear octyl, decyl, dodecyl, tetradecyl, hexadecyl or octadecyl radicals and mixtures thereof are particularly suitable. Particularly preferred alkyl glycosides contain a cocofatty alkyl group, i.e. mixtures with - essentially - R =dodecyl and R =tetradecyl.

Instead of or in addition to these surfactants, such detergents may contain other surfactants, preferably synthetic anionic surfactants of the sulfate or sulfonate type, in quantities of preferably not more than 20% by weight and, more particularly, in quantities of 0.1% by weight to 18% by weight, based on the detergent as a whole. Synthetic anionic surfactants particularly suitable for use in such detergents are C_{8-22} alkyl and/or alkenyl sulfates containing an alkali metal, ammonium or alkyl- or hydroxyalkyl-substituted ammonium ion as counter-cation. Derivatives of fatty alcohols containing in particular 12 to 18 carbon atoms and branched-chain analogs thereof, so-called oxoalcohols, are preferred. The alkyl and alkenyl sulfates may be produced in known manner by reaction of the corresponding alcohol component with a typical sulfating agent, more particularly sulfur trioxide or chlorosulfonic acid, and subsequent neutralization with alkali metall, ammonium or alkyl- or hydroxyalkyl-substituted ammonium bases. The alkyl and/or alkenyl sulfates are present in the detergents according to the invention or in the detergents used in

combination with the polyvinyl alcohol used in accordance with the invention in quantities of preferably 0.1% by weight to 20% by weight and, more preferably, 0.5% by weight to 18% by weight.

Suitable surfactants of the sulfate type also include sulfated alkoxy-
5 lation products of the alcohols mentioned, so-called ether sulfates. Ether sulfates preferably contain 2 to 30 and, more particularly, 4 to 10 ethylene glycol groups per molecule. Suitable anionic surfactants of the sulfonate type include the α -sulfoesters obtainable by reaction of fatty acid esters with sulfur trioxide and subsequent neutralization, more particularly the
10 sulfonation products derived from fatty acids containing 8 to 22 and preferably 12 to 18 carbon atoms and linear alcohols containing 1 to 6 and preferably 1 to 4 carbon atoms, and the sulfofatty acids obtainable therefrom by formal saponification.

Other optional surface-active ingredients are soaps, saturated fatty
15 acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid or stearic acid, and soaps derived from natural fatty acid mixtures, for example cocofatty acid, palm kernel oil fatty acid or tallow fatty acid. Soap mixtures of which 50% by weight to 100% by weight consist of saturated C_{12-18} fatty acid soaps and up to 50% by weight of oleic acid soap are
20 particularly preferred. Soap is preferably present in quantities of 0.1% by weight to 5% by weight. However, larger quantities of soap of generally up to 20% by weight may also be present, particularly in liquid detergents containing a polymer used in accordance with the invention.

In another embodiment, a detergent containing a polymer to be used
25 in accordance with the invention contains water-soluble and/or water-insoluble builders, more particularly selected from alkali metal aluminosilicate, crystalline alkali metal silicate with a modulus of > 1 , monomeric polycarboxylate, polymeric polycarboxylate and mixtures thereof, more particularly in quantities of 2.5% by weight to 60% by weight.

30 A detergent containing polyvinyl alcohol to be used in accordance

with the invention preferably contains 20% by weight to 55% by weight of water-soluble and/or water-insoluble, organic and/or inorganic builders. Water-soluble organic builders include in particular those from the class of polycarboxylic acids, more particularly citric acid and sugar acids, and polymeric (poly)carboxylic acids, more particularly the polycarboxylates obtainable by oxidation of polysaccharides according to International patent application **WO 93/16110**, polymeric acrylic acids, methacrylic acids, maleic acids and copolymers thereof, which may also contain small amounts of polymerizable substances with no carboxylic acid functionality in copolymerized form. The relative molecular weight of the homopolymers of unsaturated carboxylic acids is generally between 5,000 and 200,000 while the relative molecular weight of the copolymers is between 2,000 and 200,000 and preferably between 50,000 and 120,000, based on free acid. A particularly preferred acrylic acid/maleic acid copolymer has a relative molecular weight of 50,000 to 100,000. Suitable but less preferred compounds of this class are copolymers of acrylic acid or methacrylic acid with vinyl ethers, such as vinyl methyl ethers, vinyl esters, ethylene, propylene and styrene, in which the percentage content of the acid is at least 50% by weight. Other suitable water-soluble organic builders are terpolymers which contain two carboxylic acids and/or salts thereof as monomers and vinyl alcohol and/or a vinyl alcohol derivative or a carbohydrate as the third monomer. The first acidic monomer or its salt is derived from a monoethylenically unsaturated C₃₋₈ carboxylic acid and preferably from a C₃₋₄ monocarboxylic acid, more particularly (meth)acrylic acid. The second monomer or its salt may be a derivative of a C₄₋₈ dicarboxylic acid, preferably a C₄₋₈ dicarboxylic acid, maleic acid being particularly preferred. In this case, the third monomeric unit is formed by vinyl alcohol and/or preferably by an esterified vinyl alcohol. Vinyl alcohol derivatives containing an ester of short-chain carboxylic acids, for example C₁₋₄ carboxylic acids, with vinyl alcohol are particularly preferred. Preferred

terpolymers contain 60% by weight to 95% by weight and more particularly 70% by weight to 90% by weight of (meth)acrylic acid or (meth)acrylate, preferably acrylic acid or acrylate, and maleic acid or maleate and 5% by weight to 40% by weight and preferably 10% by weight to 30% by weight of vinyl alcohol and/or vinyl acetate. Terpolymers in which the ratio by weight of (meth)acrylic acid or (meth)acrylate to maleic acid or maleate is between 1:1 and 4:1, preferably between 2:1 and 3:1 and more preferably between 2:1 and 2.5:1 are most particularly preferred (both the quantities and the ratios by weight are based on the acids). The second acidic monomer or its salt may also be a derivative of an allyl sulfonic acid which is substituted in the 2-position by an alkyl group, preferably by a C₁₋₄ alkyl group, or by an aromatic group preferably derived from benzene or benzene derivatives. Preferred terpolymers contain 40% by weight to 60% by weight and, more particularly, 45 to 55% by weight of (meth)acrylic acid or (meth)acrylate, preferably acrylic acid or acrylate, 10% by weight to 30% by weight and preferably 15% by weight to 25% by weight of methallyl sulfonic acid or methallyl sulfonate and, as the third monomer, 15% by weight to 40% by weight and preferably 20% by weight to 40% by weight of a carbohydrate. This carbohydrate may be, for example, a mono-, di-, oligo- or polysaccharide, mono-, di- or oligosaccharides being preferred and sucrose being particularly preferred. Weakened points responsible for the ready biodegradability of the polymer are presumably incorporated therein through the use of the third monomer. These terpolymers may be produced in particular by the processes described in German patent **DE 42 21 381** and in German patent application **DE 43 00 772** and have a relative molecular weight of generally from 1,000 to 200,000, preferably from 200 to 50,000 and more preferably from 3,000 to 10,000. They may be used in the form of aqueous solutions, preferably in the form of 30 to 50% by weight aqueous solutions, particularly for the production of liquid detergents. All the polycarboxylic acids mentioned are generally used in

the form of their water-soluble salts, particularly their alkali metal salts.

Organic builders of the type in question are preferably present in quantities of up to 40% by weight, more preferably in quantities of up to 25% by weight and most preferably in quantities of 1% by weight to 5% by weight. Quantities near the upper limit mentioned are preferably used in paste-form or liquid, more particularly water-containing, detergents in which the cellulase mixture is present.

Suitable water-insoluble, water-dispersible inorganic builders are, in particular, crystalline or amorphous alkali metal aluminosilicates used in quantities of up to 50% by weight, preferably in quantities of not more than 40% by weight and - in liquid detergents in particular - in quantities of 1% by weight to 5% by weight. Of these builders, detergent-quality crystalline aluminosilicates, particularly zeolite NaA and optionally NaX, are preferred. Quantities near the upper limit mentioned are preferably used in solid particulate detergents. Suitable aluminosilicates contain no particles larger than 30 μm in size, at least 80% by weight preferably consisting of particles below 10 μm in size. Their calcium binding capacity which may be determined in accordance with German patent **DE 24 12 387** is in the range from 100 to 200 mg CaO per gram. Suitable substitutes or partial substitutes for the aluminosilicate mentioned are crystalline alkali metal silicates which may be present either individually or in the form of a mixture with amorphous silicates. The alkali metal silicates suitable as builders in the detergents preferably have a molar ratio of alkali metal oxide to SiO_2 of less than 0.95:1 and, more particularly, from 1:1.1 to 1:12 and may be present in amorphous or crystalline form. Preferred alkali metal silicates are sodium silicates, more particularly amorphous sodium silicates, with a molar $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:1 to 1:2.8. Amorphous alkali metal silicates such as these are commercially available, for example under the name of Portil®. Those with a molar $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:1.9 to 1:2.8 may be produced by the process according to European patent application **EP 0**

425 427. They are preferably added in solid form rather than in the form of a solution in the production process. Preferred crystalline silicates, which may be present either individually or in the form of a mixture with amorphous silicates, are crystalline layer silicates with the general formula $\text{Na}_2\text{Si}_x\text{O}_{2x+1}\text{AyH}_2\text{O}$, in which x , the so-called modulus, is a number of 1.9 to 4 and y is a number of 0 to 20, preferred values for x being 2, 3 or 4. Crystalline layer silicates which correspond to this general formula are described, for example, in European patent application **EP 0 164 514**. Preferred crystalline layer silicates are those in which x in the general formula shown above assumes a value of 2 or 3. Both β - and δ -sodium disilicates ($\text{Na}_2\text{Si}_2\text{O}_5\text{AyH}_2\text{O}$) are particularly preferred, β -sodium disilicate being obtainable for example by the process described in International patent application **WO 91/08171**. δ -Sodium silicates with a modulus of 1.9 to 3.2 may be produced in accordance with Japanese patent applications **JP 04/238 809** or **JP 04/260 610**. Substantially water-free crystalline alkali metal silicates produced from amorphous alkali metal silicates and corresponding to the above general formula where x is a number of 1.9 to 2.1, obtainable as described in European patent applications **EP 0 548 599**, **EP 0 502 325** and **EP 0 452 428**, may also be used in detergents according to the invention. Another preferred embodiment of a detergent according to the invention is characterized by the use of a crystalline sodium layer silicate with a modulus of 2 to 3 which may be obtained from sand and soda by the process according to European patent application **EP 0 436 835**. Crystalline sodium silicates with a modulus of 1.9 to 3.5, which may be obtained by the processes according to European patent **EP 0 164 552** and/or European patent application **EP 0 294 753**, are used in another preferred embodiment of detergents containing a polymer according to the invention. Their alkali metal silicate content is preferably from 1% by weight to 50% by weight and more preferably from 5% by weight to 35% by weight, based on water-free active substance. If alkali

metal aluminosilicate, more particularly zeolite, is also present as an additional builder, the alkali metal silicate content is preferably from 1% by weight to 15% by weight and more preferably from 2% by weight to 8% by weight, based on water-free active substance. In that case, the ratio by weight of aluminosilicate to silicate, based on water-free active substances, is preferably from 4:1 to 10:1. In detergents containing both amorphous and crystalline alkali metal silicates, the ratio by weight of amorphous alkali metal silicate to crystalline alkali metal silicate is preferably 1:2 to 2:1 and more preferably 1:1 to 2:1.

In addition to the inorganic builder mentioned, other water-soluble or water-insoluble inorganic substances may be used in detergents containing a polyvinyl alcohol used as soil release polymer in accordance with the invention. Alkali metal carbonates, alkali metal hydrogen carbonates and alkali metal sulfates and mixtures thereof are suitable in this regard. This additional inorganic material may be present in quantities of up to 70% by weight, but is preferably absent altogether.

The detergents may additionally contain other constituents typically encountered in detergents and cleaners. These optional constituents include, in particular, other enzymes, enzyme stabilizers, bleaching agents, bleach activators, heavy metal complexing agents, for example aminopolycarboxylic acids, aminohydroxypolycarboxylic acids, polyphosphonic acids and/or aminopolyphosphonic acids, redeposition inhibitors, for example cellulose ethers, dye transfer inhibitors, for example polyvinyl pyrrolidone or polyvinyl pyridine-N-oxide, foam inhibitors, for example organopolysiloxanes or paraffins, solvents and optical brighteners, for example stilbene disulfonic acid derivatives. Detergents containing a polymer according to the invention preferably contain up to 1% by weight and, more particularly, 0.01% by weight to 0.5% by weight of optical brighteners, more particularly compounds from the class of substituted 4,4'-bis-(2,4,6-triamino-s-triazinyl)-stilbene-2,2'-disulfonic acids, up to 5% by

weight and, more particularly 0.1% by weight to 2% by weight of heavy metal complexing agents, more particularly aminoalkylene phosphonic acids and salts thereof, up to 3% by weight and, more particularly, 0.5% by weight to 2% by weight of redeposition inhibitors and up to 2% by weight and, more particularly, 0.1% by weight to 1% by weight of foam inhibitors, the percentages by weight mentioned all being based on the detergent as a whole.

Besides water, preferred solvents, which may be used in particular in liquid detergents containing a polymer used in accordance with the invention, are water-miscible solvents. These include lower alcohols, for example ethanol, propanol, isopropanol and the isomeric butanols, glycerol, lower glycols, for example ethylene and propylene glycol, and the ethers derived from compounds belonging to the classes mentioned. The polymers used in accordance with the invention are generally present in dissolved or suspended form in such liquid detergents

Enzymes optionally present are preferably selected from the group consisting of protease, amylase, lipase, hemicellulase, oxidase, peroxidase or mixtures thereof. Protease obtained from microorganisms, such as bacteria or fungi, is particularly suitable. It may be obtained by known fermentation processes from suitable microorganisms which are described, for example, in **DE-OSS 19 40 488**, **20 44 161**, **22 01 803** and **21 21 397**, in **US-PSS 3,632,957** and **4,264,738**, in European patent application **EP 006 638** and in International patent application **WO 91/02792**. Proteases are commercially available, for example, under the names of **BLAP®**, **Savinase®**, **Esperase®**, **Maxatase®**, **Optimase®**, **Alcalase®**, **Durazym®** or **Maxapem®**. The lipase suitable for use in accordance with the invention may be obtained from *Humicola lanuginosa*, as described for example in European patent applications **EP 0 258 068**, **EP 0 305 216** and **EP 0 341 947**, from bacillus species, as described for example in International patent application **WO 91/16422** or European patent application **EP 0 384 717**,

from pseudomonas species, as described for example in European patent applications **EP 0 468 102**, **EP 0 385 401**, **EP 0 375 102**, **EP 0 334 462**, **EP 0 331 376**, **EP 0 330 641**, **EP 0 214 761**, **EP 0 218 272** or **EP 0 204 284** or in International patent application **WO 90/10695**, from fusarium species, as described for example in European patent application **EP 0 130 064**, from rhizopus species, as described for example in European patent application **EP 0 117 553**, or from aspergillus species, as described for example in European patent application **EP 0 167 309**. Suitable lipases are commercially available, for example, under the names of Lipolase®, Lipozym®, Lipomax, Amano® Lipase, Toyo Jozo® Lipase, Meito® Lipase and Diosynth® Lipase. Suitable amylases are commercially obtainable, for example, under the names of Maxamyl®, Termamyl® and Purafect® OxAm. The cellulase used may be an enzyme obtainable from bacteria or fungi which has an optimum pH preferably in the mildly acidic to mildly alkaline range of 6 to 9.5. Such cellulases are known, for example, from **DE-OSS 31 17 250**, **DE 32 07 825**, **DE 32 07 847**, **DE 33 22 950** and from European patent applications **EP 0 265 832**, **EP 0 269 977**, **EP 0 270 974**, **EP 0 273 125** and **EP 0 339 550**.

Typical enzyme stabilizers which may optionally be present, particularly in liquid detergents, include aminoalcohols, for example mono-, di-, tri-ethanolamine and -propanolamine and mixtures thereof, lower carboxylic acids as known, for example, from European patent applications **EP 0 376 705** and **EP 0 378 261**, boric acid and alkali metal borates, boric acid/carboxylic acid combinations as known, for example, from European patent application **EP 0 451 921**, boric acid esters as known, for example, from International patent application **WO 93/11215** or European patent application **EP 0 511 456**, boric acid derivatives as known, for example, from European patent application **EP 0 583 536**, calcium salts, for example the calcium/formic acid combination known from European patent **EP 0 028 865**, magnesium salts as known, for example, from European patent

application **EP 0 378 262** and/or sulfur-containing reducing agents as known, for example, from European patent applications **EP 0 080 748** or **EP 0 080 223**.

Suitable foam inhibitors include long-chain soaps, more particularly
5 behenic soap, fatty acid amides, paraffins, waxes, microcrystalline waxes, organopolysiloxanes and mixtures thereof which may additionally contain microfine, optionally silanized or otherwise hydrophobicized silica. For use in particulate detergents, these foam inhibitors are preferably fixed to granular water-soluble supports, as described for example in **DE-OS 34 36**
10 **194**, in European patent applications **EP 0 262 588**, **EP 0 301 414** or **EP 0 309 931** or in European patent **EP 0 150 386**.

A detergent containing a polymer used in accordance with the invention may also contain redeposition inhibitors. The function of redeposition inhibitors is to keep the soil detached from the fibers
15 suspended in the wash liquor. Water-soluble, generally organic colloids are suitable for this purpose, including for example the water-soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ether carboxylic acids or ether sulfonic acids of starch or cellulose or salts of acidic sulfuric acid esters of cellulose or starch. Water-soluble polyamides containing acidic
20 groups are also suitable for this purpose. Soluble starch preparations and other starch products than those mentioned above, for example partly hydrolyzed starch, may also be used. Sodium carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose and mixtures thereof are preferably used.

25 Another embodiment of a detergent containing a soil release polymer to be used in accordance with the invention contains peroxygen-based bleaching agents, more particularly in quantities of 5% by weight to 70% by weight, and optionally bleach activator, more particularly in quantities of 2% by weight to 10% by weight. Suitable bleaching agents
30 are the per compounds generally used in detergents, such as hydrogen

peroxide, perborate (which may be present as tetra- or monohydrate), percarbonate, perpyrophosphate and persilicate which are generally present as alkali metal salts, more particularly as sodium salts. Such bleaching agents are present in detergents according to the invention in quantities of preferably up to 25% by weight, more preferably in quantities of up to 15% by weight and most preferably in quantities of 5% by weight to 15% by weight, based on the detergent as a whole. The optional bleach activator component may be selected from the N- or O-acyl compounds normally used, for example polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine, acylated glycolurils, more particularly tetraacetyl glycoluril, N-acylated hydantoins, hydrazides, triazoles, urazoles, diketopiperazines, sulfonyl amides and cyanurates, and from carboxylic anhydrides, more particularly phthalic anhydride, carboxylic acid esters, more particularly sodium nonanoyl or isononanoyloxybenzene sulfonate, and acylated sugar derivatives, more particularly pentaacetyl glucose. To avoid interaction with the per compounds in storage, the bleach activators may be coated or granulated in known manner with membrane materials, tetraacetyl ethylenediamine granulated with carboxymethyl cellulose and having average particle sizes of 0.01 mm to 0.8 mm, which may be produced for example by the process described in European patent **EP 0 037 026**, and/or granulated 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine, which can be produced by the process described in East German patent **DD 255 884**, being particularly preferred. The bleach activators in question are present in detergents in quantities of preferably up to 8% by weight and more preferably in quantities of 2% by weight to 6% by weight, based on the detergent as a whole.

In one preferred embodiment, a detergent in which soil release polymer to be used in accordance with the invention is incorporated is particulate and contains 20% by weight to 55% by weight of inorganic builder, up to 15% by weight and more particularly from 2% by weight to

12% by weight of water-soluble organic builder, 2.5% by weight to 20% by weight of synthetic anionic surfactant, 1% by weight to 20% by weight of nonionic surfactant, up to 25% by weight and more particularly from 1% by weight to 15% by weight of bleaching agent, up to 8% by weight and more particularly from 0.5% by weight to 6% by weight of bleach activator and up to 20% by weight and more particularly from 0.1% by weight to 15% by weight of inorganic salts, more particularly alkali metal carbonate and/or sulfate.

Another preferred embodiment is a liquid detergent containing from 5% by weight to 35% by weight of water-soluble organic builder, up to 15% by weight and more particularly from 0.1 to 5% by weight of water-insoluble inorganic builder, up to 25% by weight and more particularly from 0.5% by weight to 15% by weight of synthetic anionic surfactant, from 1% by weight to 45% by weight and more particularly from 15% by weight to 25% by weight of nonionic surfactant, up to 25% by weight and more particularly from 4% by weight to 15% by weight of soap and up to 30% by weight and more particularly from 1% by weight to 25% by weight of water and/or water-miscible solvent.

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Examples

Example 1

Particulate detergents (E1 to E6) were produced from the polyvinyl alcohols listed in Table 1 by incorporation of the other ingredients. The detergents, which contained 2% by weight of the particular polyvinyl alcohol (P1 to P6) and 7% by weight of ethoxylated fatty alcohol, 1% by weight of soap, 20% by weight of alkyl benzenesulfonate, 35% by weight of zeolite NaA, 7% by weight of sodium citrate, 7% by weight of polymeric polycarboxylate, 5% by weight of sodium carbonate, 2% by weight of enzyme granules (protease, lipase, cellulase, amylase), balance to 100% water and neutral salts, were tested for their performance against greasy soils. In

addition, a detergent (V1) with the same composition as above, except that the polyvinyl alcohol was missing, and a detergent V1 (E7) packed in a film bag of polyvinyl alcohol (the polyvinyl alcohol film making up 2% by weight of the product as a whole) were tested for comparison. To this end, the standardized test soils **A** (lipstick) and **B** (creme rouge) shown in the following Table on swatches of cotton, polyester and polyester/cotton blend were washed together with 3.5 kg of clean ballast washing at 40°C in a Miele Novotronic® W918 washing machine (one-wash program, water hardness 16°dH, detergent dose 80 g). The test swatches were then dried and their degree of cleanness was determined by reflectance measurement (at 460 nm). The increases in reflectance (ddE) are shown in Tables 2, 3 and 4 below.

Table 1:

Polyvinyl alcohols

	Molecular weight	Degree of hydrolysis [% by weight]
P1	14,000	83
P2	67,000	88
P3	61,000	98
P4	160,000	88
P5	28,000	71
P6	195,000	90

Table 2

Increase in reflectance (ddE) for soils on cotton

	Soil	
Detergent	A	B
E1	54.8	n.d.
E2	52.0	n.d.
E3	54.1	n.d.
E4	50.5	33.0
E5	49.5	32.6
E6	48.6	n.d.
E7	48.9	33.0
V1	48.2	31.9

Table 3:

Increase in reflectance (ddE) for soils on cotton/polyester

	Soil	
Detergent	A	B
E1	50.5	31.1
E2	45.3	31.2
E3	42.1	26.9
E4	53.0	32.6
E5	52.2	31.6
E6	n.d.	29.8
E7	48.3	32.6
V1	41.0	24.8

Table 4:

Increase in reflectance (ddE) for soils on polyester

	Soil	
Detergent	A	B
E1	18.4	26.1
E2	n.d.	n.d.
E3	16.8	24.3
E4	31.7	39.4
E5	32.0	38.8
E6	25.8	29.0
E7	30.6	35.0
V1	16.1	22.3

n.d.: not determined

Example 2

As Example 1, except that polyvinyl alcohols (P9, P10) obtained by partial acetylation of the polyvinyl alcohol Polyviol 05/290 (P8) (a Wacker product) were used. The partly acetylated polyvinyl alcohols P11 and P12 are blown films with the following composition: P11: 83.0% Polyviol 05/290, 11.3% glycerol, 5.1% sorbitol, 0.5% Aerosil, 0.1% stearic acid; P12: 37.6% Polyviol 05/290, 37.6% Mowilith 8/88 (polyvinyl alcohol, a Clariant product), 16.7% glycerol, 4.6% sorbitol, 2.8% distilled water, 0.5% Aerosil, 0.2% stearin. The mixtures were processed and granulated at 50 r.p.m. The granules obtained were processed in a film blowing machine (Brabender single-screw kneader). The temperature profile from the feed zone to the die was adjusted as follows: heating zones 1 to 6, 180, 175, 160, 150, 120, 120°C. The screw was driven at 50 r.p.m. which produced a torque of 80 Nm. A film take-of rate of 1.3 was adjusted. E8 to E12 are the particulate detergents containing the particular polyvinyl alcohol (P8 to P12) obtained

as in Example 1 by incorporation of the other ingredients. In addition, a detergent (V2) with the composition described in Example 1, but without the polyvinyl alcohol addition, was tested for comparison.

Table 5:

Partly acetylated polyvinyl alcohols

	Molecular weight	Degree of hydrolysis [% by weight]
P8	28,000	73
P9	n.d.	69
P10	n.d.	63
P11	14,000	69
P12	67,000	63

Table 6

Increase in reflectance (ddE) for soils on cotton

	Soil	
Detergent	A	B
E8	65.1	39.7
E9	68.3	41.4
E10	63.8	38.5
E11	64.1	39.4
E12	63.5	42.2
V2	52.4	36.3

Table 7:

Increase in reflectance (ddE) for soils on cotton/polyester

	Soil	
Detergent	A	B
E8	68.8	41.8
E9	72.4	40.3
E10	71.2	41.9
E11	72.2	39.3
E12	74.4	42.3
V2	64.2	37.2

Table 8:

Increase in reflectance (ddE) for soils on polyester

	Soil	
Detergent	A	B
E8	50.0	36.0
E9	49.6	36.2
E10	52.0	40.3
E11	51.4	37.2
E12	51.3	41.9
V2	36.1	25.6

n.d.: not determined

The invention may be varied in any number of ways as would be apparent to a person skilled in the art and all obvious equivalents and the like are meant to fall within the scope of this description and claims. The

5 description is meant to serve as a guide to interpret the claims and not to limit them unnecessarily.

CLAIMS

1. The use of polyvinyl alcohol for boosting the cleaning performance of detergents in the washing of textiles.

5 2. The use of polyvinyl alcohol for boosting the cleaning performance of detergents in the washing of textiles consisting of or containing cotton.

3. The use claimed in claim 1 or 2, wherein the polyvinyl alcohol has a molecular weight of 3000 g/mole to 320,000 g/mol.

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4. The use as claimed in claim 1 or 2, wherein the polyvinyl alcohol has a molecular weight in the range from 8000 g/mole to 200,000 g/mole.

15 5. The use claimed in any of claims 1 to 4, wherein the polyvinyl alcohol is a partly saponified polyvinyl alcohol ester with a residual content of acyl groups of up to about 80% by weight.

6. The use as claimed in claim 5, wherein the polyvinyl alcohol is a polyvinyl acetate.

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7. The use as claimed in any of claims 1 to 6, wherein the polyvinyl alcohol has a residual content of acetyl groups.

25 8. The use as claimed in claims 5, 6 or 7, wherein the residual content is in the range of from 10% by weight to 70% by weight.

9. The use claimed in any of claims 1 to 8, wherein the polyvinyl alcohol is used together with surfactant, the ratio by weight of surfactant to polyvinyl alcohol being in the range from 20:1 to 5:1.

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10. The use as claimed in claim 9, wherein the ratio is in the range of from 15:1 to 7:1.
11. A laundry detergent comprising polyvinyl alcohol and 5% by weight
5 to 30% by weight of surfactant.
12. A laundry detergent as claimed in claim 11, wherein there is present 10% by weight to 25% by weight of surfactant.
- 10 13. A laundry detergent as claimed in claim 11 or 12, wherein there is present 0.1% by weight to 10% by weight of polyvinyl alcohol.
14. A laundry detergent as claimed in claim 13, wherein there is present 1% by weight to 4% by weight of polyvinyl alcohol.
- 15 15. A laundry detergent as claimed in any one claims 11 to 14, wherein the ratio by weight of surfactant to polyvinyl alcohol is from 20:1 to 5:1.
16. A laundry detergent as claimed in claim 15, wherein the ratio by
20 weight of surfactant to polyvinyl alcohol is from 15:1 to 7:1.
17. A laundry detergent as claimed in any of claims 11 to 16, wherein at least part of the polyvinyl alcohol present is in the form of a bag of polyvinyl alcohol or polyvinyl alcohol-containing material which holds the rest of the
25 detergent ingredients and optionally the rest of the polyvinyl alcohol.
18. A laundry detergent as claimed in any of claims 11 to 17, wherein the bulk density is from 600 g/l to 1200 g/l.

19. A laundry detergent as claimed in claim 18, wherein the range is from 700 g/l to 1000 g/l.

20. A laundry detergent as claimed in any of claims 13 to 19, wherein
5 the detergent has a mean particle size of 0.8 mm to 6 mm.

21. A laundry detergent as claimed in claim 20, wherein the mean particle size is 0.8 mm to 6 mm.