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(54) **Detergent additives and detergent compositions containing them.**

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Description

The present invention relates to additives for detergent compositions, and to detergent compositions containing them. These compositions are particularly, but not essentially, adapted for fabric washing. The invention relates more particularly to substantially phosphate-free detergent compositions.

Fabric washing compositions conventionally contain phosphate detergency builders such as sodium tripolyphosphate. In some circumstances it is thought that the use of phosphates in detergent compositions can lead to environmental problems in waste waters. There is therefore a desire to reduce the level of phosphorus, or to eliminate it altogether, in detergent compositions.

Water-insoluble aluminosilicate ion exchange materials have been suggested as alternative builders to phosphates; see, for example, GB 1,473,201 and GB 1,473,202 (Henkel). It has been found in practice, however, that these aluminosilicate materials, even in large amounts, tend to be undesirably slow in their exchange of cations, especially at low temperatures, resulting in inferior detergency. It has accordingly been suggested that supplementary water-soluble builders should be used in combination with these aluminosilicates to raise the detergency to an acceptable level. These supplementary builders are generally materials that are efficiency sequestrant builders in their own right, for example, alkali metal tripolyphosphates, nitrilotriacetates and poly-α-hydroxyacrylates. High levels of these materials are, however, not generally desirable in detergent compositions for cost of environmental reasons.

GB 1,429,143, GB 1,501,498 and GB 1,516,865 (Procter & Gamble) disclose detergent compositions containing aluminosilicate together with sodium carbonate as supplementary builder.

We have now discovered that, surprisingly, the detergency of aluminosilicate-built detergent products can be substantially boosted by partially replacing the aluminosilicate by a certain type of organic precipitant builder having a divalent anion. Replacement of, for example, 15 to 30% of the aluminosilicate by such an organic precipitant builder has been found to give detergency results comparable to those obtainable using combinations of zeolite and sodium tripolyphosphate as builders.

It is known that the detergency builder properties of aluminosilicates are enhanced by the addition of water-soluble complexing agents such as sodium tripolyphosphate. This effect has been explained in terms of the so-called "carrier molecule model": see, for example, P. Berth, J. Am. Oil Chemists' Soc *55*, 52—53 (1978). The complexing agent is able to take up polyvalent water hardness ions (notable Ca^{2+}, but also Mg^{2+}) from solid surfaces (such as the surface of a textile fibre) and pass them on to the aluminosilicate ion-exchanger after transport through the aqueous medium. The complexing agent forms a chelate complex with the hardness ion which on arrival at the surface of the aluminosilicate dissociates.

It is not easy to envisage a similar mechanism with precipitant builders, since these remove hardness ions from the wash liquor by the virtually irreversible formation of a precipitate (insoluble calcium or magensium salt).

It is thus surprising that aluminosilicate/organic precipitant combinations can give building properties comparable to those of aluminosilicate/complexing agent combinations.

Attempts have been made to use the commonest organic precipitant builder, soap, as a supplementary builder for zeolites, but detergency benefits have been obtained only at impractically high builder concentrations (8 g/l and above). This is a consequence of a low weight effectiveness of soaps when used as builders; since the soap anion is monovalent two moles of soap are consumed by each gram ion of Ca^{2+} or Mg^{2+}.

GB 1,545,801 (Procter & Gamble) discloses a spray-dried granular detergent composition comprising from 1 to 40% by weight of an organic detergent component; from 3 to 25% by weight of a water-insoluble crystalline aluminosilicate ion-exchange material of the formula:

$$Na_{12}[AlO_2 \cdot SiO_2]_{12}xH_2O$$

wherein x is an integer of from 20 to 30; from 5 to 35% by weight of a phosphate builder; and from 5 to 25% of an alkali metal silicate. The organic detergent component may be *inter alia* a water-soluble salt of a C_6 to C_{29} α-sulphocarboxylic acid.

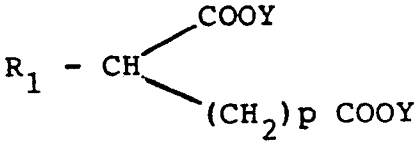
The present invention provides a detergent composition comprising:

(a) from 3 to 90% by weight of one or more detergent-active agents, and

(b) from 10 to 97% by weight of a detergent additive (builder component) consisting essentially of

(i) from 25 to 97% by weight, based on the detergent additive, of a crystalline or amorphous aluminosilicate cation-exchange material, and

(ii) from 3% to 75% by weight of an organic precipitant builder having the formula I



$$R_1 - CH \begin{cases} COOY \\ (CH_2)p\ COOY \end{cases} \qquad (I)$$

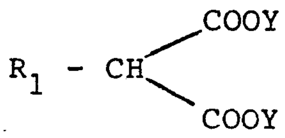
wherein:

R_1 is a C_{10}—C_{24} alkyl, alkenyl, arylalkyl or alkylaryl group;
Y is hydrogen or a solubilising cation; and
p is 0 or 1.

The organic precipitant builder is a water-soluble material that reacts with Ca^{2+} ions, and preferably also with Mg^{2+} ions, in a 1:1 stoichiometric ratio, to form an insoluble salt. The solubility product of the calcium salt of the organic precipitant builder is preferably less than 10^{-8}.

Especially preferred classes of compounds within the general formula I are the following:

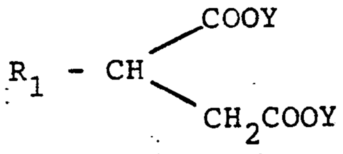
(i) substituted malonates of the formula II:



(II)

and

(ii) substituted succinates of the formula III:



(III)

Compounds of the formulae II and III are described, for example, in GB 1,293,753, GB 1,342,247 and GB 1,342,340 (Unilever). Examples of such compounds include disodium dodecyl malonate (C_{12}-AKM), disodium hexadecenyl succinate ($C_{16:1}$-AKS), and disodium mixed C_{15}—C_{18} succinate (C_{15-18}-AKS).

The aluminosilicate cation exchange material is preferably crystalline or amorphous material having the general formula:

$$(Cat_{2/n}O)_x . Al_2O_3(SiO_2)_y zH_2O$$

wherein Cat is a cation having valency n that is exchangeable with calcium (e.g. Na^+ or K^+); x is a number from 0.7—1.5; y is a number from 1.3—4; and z is such that the bound water content is from 10% to 28% by weight.

Preferably a crystalline material is used which can be described by the unit cell content:

$$Na_x(AlO_2)_x . (SiO_2)_y \, zH_2O$$

wherein x and y are integers of at least 6, the ratio of x to y being in the ratio of 1:1 to 1:2; and z is such that the bound water content is from 10% to 28% by weight.

The aluminosilicate preferably has a particle size of from 0.1 to 100 micrometres, ideally between 0.1 to 10 micrometres, and an ion exchange capacity of at least 200 mg $CaCO_3$ per gram of aluminosilicate (anhydrous basis).

In a preferred embodiment the water-insoluble aluminosilicate is a crystalline material having the formula described by the unit cell content:

$$Na_x[(AlO_2)_x . (SiO_2)_y]zH_2O$$

wherein x and y are integers of at least 6, the ratio of x to y being in the range of 1:1 to 1:2; and z is such that the bound water content is from 10% to 28% by weight.

The aluminosilicate preferably has a particle size of from 0.1 to 100 micrometres, ideally between 0.1 and 10 micrometres, and an ion exchange capacity of at least 200 mg $CaCO_3$ per gram of aluminosilicate (anhydrous basis).

In a preferred embodiment the water-insoluble aluminosilicate is a crystalline material having the formula described by the unit cell content:

$$Na_{12}(AlO_2)_{12} . (SiO_2)_{12} . zH_2O$$

wherein z is from 20 to 30, preferably about 27.

An example of this material is the commercially available product known as Zeolite type A, which is typically:

$$Na_2O . Al_2O_3 . 2SiO_2 . {}^\wedge 4.5H_2O$$

and is also described by the unit cell content:

$$Na_{12}[(AlO_2)_{12}.(SiO_2)_{12}].27H_2O.$$

The detergent composition of the invention contains from 10% to 97% by weight of the specified detergent additive, preferably from 12% to 80%, more preferably from 15% to 70%, and especially from 16% to 67%.

Since the detergent additive contains from 25% to 97% by weight of aluminosilicate, the aluminosilicate content of the detergent composition can range from 2.5% to 94%. An aluminosilicate content of from 10% to 60%, especially from 12% to 55%, is especially preferred.

Similarly, the content of organic precipitant builder can range from 0.3% to 73%, a range of from 1% to 30%, especially from 3% to 17%, being especially preferred.

The detergent compositions of the present invention are preferably substantially free of inorganic phosphate. This is highly desirable for the environmental reasons mentioned earlier. Compositions according to the invention containing no inorganic phosphate have been found to exhibit detergency properties comparable to those of sodium tripolyphosphate-built products.

If desired, however, the compositions may contain inorganic phosphate, but preferably at a level not exceeding 10% based on the whole product. Any phosphate present may, for example, be in the form of alkali metal (preferably sodium) tripolyphosphate, orthophosphate pyrophosphate or polymeric phosphate.

The organic precipitant builder constitutes from about 3% to about 75% by weight of the builder mix (detergent additive) present in the detergent composition of the invention, preferably from about 10% to about 60% and especially from about 15% to about 30%.

The detergent compositions of the invention may if desired contain further non-phosphate builders. The compositions may for example contain organic sequestrant builders in addition to the organic precipitants, for example, as disclosed in our co-pending Application No. 82 303 674.4 (EP 70190) entitled "Detergent additives and detergent compositions containing them". Organic sequestrant builders are water-soluble materials which form soluble complexes with calcium, preferably with pK_{Ca} greater than 3.0, preferably greater than 4.0 and more preferably greater than 4.5. Some sequestrant builders also form complexes with magnesium, preferably with pK_{Mg} greater than 4.0.

Examples of such materials include alkali metal (especially sodium) salts of the following acids: nitrilotriacetic acid, ethylenediamine tetracetic acid, polyacrylic acid, poly(α-hydroxyacrylic) acid, carboxymethyloxymalonic acid, carboxymethyloxysuccinic acid, oxydiacetic acid, oxydisuccinic acid, citric acid, dipicolinic acid and many more. The polyacetal carboxylates disclosed in US 4,144,126 and US 4,146,495 (Monsanto) and the oxidised polysaccharides disclosed in GB 1,330,121, GB 1,330,122 and GB 1,330,123 (Unilever) may also advantageously be used.

The detergent composition of the invention necessarily includes from 3% to 90% by weight, preferably from 5% to 40% by weight, more preferably from 10% to 25% by weight, of detergent-active material which may comprise synthetic anionic, nonionic, amphoteric or zwitterionic detergent compounds or mixtures thereof. Many suitable detergent-active compounds are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred detergent compounds which can be used are synthetic anionic and nonionic compounds. The former are usually water soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl suphates, especially those obtained by sulphating higher (C_8—C_{18}) alcohols produced from example from tallow or coconut oil; sodium and potassium alkyl (C_9—C_{20}) benzene sulphates, particularly sodium linear secondary alkyl (C_{10}—C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_9—C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8—C_{20}) with sodium bisulphate and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}—C_{20} alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}—C_{15}) alkyl benzene sulphonates and sodium (C_{16}—C_{18}) alkyl sulphates.

Examples of suitable nonionic detergent compounds which may be used include in particular the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6—C_{22}) phenols, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8—C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 6 to 30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Mixtures of detergent compounds, for example mixed anionic or mixed anionic and nonionic compounds may be used in the detergent compositions, particularly in the latter case to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic washing machines. Anionic and nonionic detergent compounds are advantageously used together in ratios of from 3:1 to 1.5:1.

Amounts of amphoteric or zwitterionic detergent compounds can also be used in the compositions of the invention but this is not normally desired due to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and/or nonionic detergent compounds.

If desired, the composition of the invention may also include soap. The presence of small amounts of soap is beneficial with respect to lather control and detergency. Soaps which may be used are especially the sodium or less desirably the potassium, salts of C_{10}—C_{24} fatty acids. Soaps based mainly on the longer-chain fatty acids within the range, that is to say, with at least half of the soap having a chain length of C_{16} or more, are especially preferred. This preferred chain length distribution may be conveniently obtained by using soaps from natural sources such as tallow, palm oil or rapeseed oil, which may be hardened if desired, with lesser amounts of other, shorter-chain soaps prepared from nut oils such as coconut oil or palm kernel oil.

According to a preferred embodiment of the invention, the detergent composition also contains a bleach system.

The bleach system preferably comprises a peroxy bleach compound which is an inorganic persalt, which is preferably used in conjunction with an activator therefor. The persalt may be, for example, sodium perborate (either the monohydrate or the tetrahydrate) or sodium percarbonate. The activator makes the bleaching more effective at lower temperatures, i.e. in the range from ambient temperature to about 60°C, so that such bleach systems are commonly known as low-temperature bleach systems and are well known in the art. The inorganic persalt acts to release active oxygen in solution, and the activator is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than can be obtained by use of the peroxy bleach compound alone. The ratio by weight of the peroxy bleach compound to the activator is generally from about 20:1 to about 1:1, preferably about 15:1 to about 2:1.

The detergent composition of the invention preferably contains from about 5% to about 30% by weight of the peroxy bleach compound, and about 0.1 to about 15% by weight of the activator. The total amount of the bleach system ingredients preferably lies within the range of from 5% to 35% by weight, especially from about 6% to about 30% by weight.

Typical examples of suitable peroxy bleach compounds are alkali metal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persilicates and perphosphates, of which sodium perborate is preferred.

Activators for peroxy bleach compounds have been amply described in the literature, including British patents 836,988, 855,735, 907,356, 907,358, 970,950, 1,003,310 and 1,246,339, US patents 3,332,882 and 4,128,494, Canadian patent 844,481 and South African patent 68/6,344. Specific suitable activators include:

(a) N-diacylated and N,N'-polyacylated amines, such as N,N,N',N'-tetraacetyl methylene diamine and N,N,N',N'-tetraacetyl ethylene diamine, N,N-diacetylaniline, N,N-diacetyl-p-toluidine; 1,3-diacylated hydantoins such as, for example, 1,3-diacetyl-5,5-dimethyl hydantoin and 1,3-dipropionyl hydantoin; α-acetoxy-(N,N')-polyacylmalonamide, for example α-(N,N')-diacetylmalonamide;

(b) N-alkyl-N-sulphonyl carbonamides, for example the compounds N-methyl-N-mesyl-acetamide, N-methyl-N-mesyl-benzamide, N-methyl-N-mesyl-p-nitrobenzamide, and N-methyl-N-mesyl-p-methoxybenzamide;

(c) N-acylated cyclic hydrazides, acylated triazones or urazoles, for example monoacetylmaleic acid hydrazide;

(d) O,N,N-trisubstituted hydroxylamines, such as O-benzoyl-N,N-succinyl hydroxylamine, O-acetyl-N,N-succinyl hydroxylamine, O-p-methoxybenzoyl-N,N-succinyl-hydroxylamine, O-p-nitrobenzoyl-N,N-succinyl-hydroxylamine and O,N,N-triacetyl hydroxylamine;

(e) N,N'-diacyl-sulphurylamides, for example N,N'-dimethyl-N,N'-diacetyl-sulphurylamide and N,N'-diethyl-N,N'-dipropionyl sulphurylamide;

(f) Triacylcyanurates, for example triacetyl cyanurate and tribenzoyl cyanurate;

(g) Carboxylic acid anhydrides, such as benzoic anhydride, m-chloro-benzoic anhydride, phthalic anhydride, 4-chloro-phthalic anhydride;

(h) Sugar esters, for example glucose pentaacetate;

(i) 1,3-diacyl-4,5-diacyloxy-imidazolidine, for example 1,3-diformyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5-dipropionyloxy-imidazoline;

(j) Tetraacetylglycoluril and tetrapropionylglycoluril;

(k) Diacylated 2,5-diketopiperazine, such as 1,4-diacetyl-2,5-diketopiperazine, 1,4-dipropionyl-2,5-diketopiperazine and 1,4-dipropionyl-3,6-dimethyl-2,5-diketopiperazine;

(l) Acylation products of propylenediurea or 2,2-dimethylpropylenediurea (2,4,6,8-tetraaza-bicyclo-

(3,3,1)-nonane-3,7-dione or its 9,9-dimethyl derivative), especially the tetraacetyl- or the tetrapropionylpropylenediurea or their dimethyl derivatives;

(m) Carbonic acid esters, for example the sodium salts of p-(ethoxycarbonyloxy)-benzoic acid and p-(propoxycarbonyloxy)-benzenesulphonic acid;

(n) α-acyloxy-(N,N')-polyacyl malonamides, such as α-acetoxy-(N,N')-diacetyl malonamide.

The N-diacylated and N,N'-polyacylated amines mentioned under (a) are of special interest, particularly N,N,N',N'-tetra-acetyl-ethylenediamine (TAED).

It is preferred to use the activator in granular form, preferably wherein the activator is finely divided as described in GB 2,053,998B (Unilever). Specifically, it is preferred to have an activator of an average particle size of less than 150 micrometres, which gives significant improvement in bleach efficiency. The sedimentation losses, when using an activator with an average particle size of less than 150 µm, are substantially decreased. Even better bleach performance is obtained if the average particle size of the activator is less than 100 µm. However, too small a particle size gives increased decomposition, dust-formation and handling problems, and although particle sizes below 100 µm can provide for an improved bleaching efficiency, it is desirable that the activator should not have more than 20% by weight of particles with a size of less than 50 µm. On the other hand, the activator may have a certain amount of particles of a size greater than 150 µm, but it should not contain more than 5% by weight of particles >300 µm, and not more than 20% by weight of particles >200 µm, preferably >150 µm. It is to be understood that these particle sizes refer to the activator present in the granules, and not to the granules themselves. The latter have a particle size, the major part of it ranging from 100 to 2000 µm, preferably 250 to 1000 µm. Up to 5% by weight of granules with a particle size of >1700 µm and up to 10% by weight of granules <250 µm is tolerable. The granules incorporating the activator, preferably in this finely-divided form, may be obtained by granulating a suitable carrier material, such as sodium tripolyphosphate and/or potassium tripolyphosphate with activator particles of the required size. Other granulation methods, e.g. using organic and/or inorganic granulation aids, can also be usefully employed. The granules can be subsequently dried, if required. Basically, any granulation process is applicable, as long as the granule contains the activator, and as long as the other materials present in the granule do not negatively affect the activator.

It is particulalry preferred to include in the detergent compositions a stabiliser for the bleach system, for example ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate. These stabilisers can be used in acid or salts form, especially in calcium, magnesium, zinc or aluminium salt form, as described in GB 2,048,930B (Unilever).

Apart from the components already mentioned, the detergent compositions of the invention can contain any of the conventional additives in the amounts in which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids; lather depressants such as alkyl phosphates, silicones, or alkyl phosphonic acids incorporated in petroleum jelly, wax or mineral oil; anti-redeposition agents such as sodium carboxymethylcellulose and cellulose ethers; fabric softening agents; inorganic salts such as sodium sulphate and sodium carbonate; and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases.

It may be desirable to include in the composition an amount of an alkali metal silicate, particularly sodium ortho-, meta- or preferably neutral or alkaline silicate. The presence of such alkali metal silicates at levels of at least about 1%, and preferably from about 5% to about 15% by weight of the composition, is advantageous in decreasing the corrosion of metal parts in washing machines, besides giving processing benefits and generally improved powder properties. The more highly alkaline ortho- and metasilicates would normally only be used at lower amounts within this range, in admixture with the neutral or alkaline silicates.

The composition of the invention is preferably alkaline, but not too strongly alkaline as this could result in fabric damage and also be hazardous for domestic usage. In practice the composition should desirably give a pH of from about 8.5 to about 11 in use in aqueous wash solution. It is preferred in particular for domestic products to have a pH of from about 9.0 to about 10.5 as lower pH's tend to be less effective for optimum detergency building, and more highly alkaline products can be hazardous if misused. The pH is measured at the lowest normal usage concentration of 0.1% w/v of the product in water of 12°H (Ca), (French permanent hardness, calcium only) at 50°C so that a satisfactory degree of alkalinity can be assured in use at all normal product concentrations. If necessary, up to 10% by weight of alkali metal carbonate, preferably sodium carbonate, may be included in order to raise the pH and to maintain adequate buffer capacity in the presence of acid soils.

If carbonate or phosphates are present it may be desirable to include in the composition of the invention one or more antideposition agents, to decrease any tendency to form inorganic deposits on washed fabrics. The amount of any such antideposition agent is normally from about 0.1% to about 5% by weight, preferably from about 0.2% to about 1.5% by weight of the composition. The preferred antideposition agents are anionic polyelectrolytes, especially polymeric aliphatic carboxylates, or organic phosphonates.

The detergent compositions of the invention should desirably be in free-flowing particulate, for example, powdered or granular form, and can be produced by any of the techniques commonly employed in the manufacture of such washed compositions, for example, by slurry-making and spray-drying processes. It is preferred that the process used to form the compositions should result in a product having a moisture content of not more than about 12%, more preferably from about 4% to about 10% by weight.

The detergent compositions of the invention may also be in the form of bars or tablets, or in liquid form.

The invention will now be illustrated by the following non-limiting Examples.

Examples

In the Examples that follow, the detergencies of wash liquors incorporating various builder systems were compared by measuring the reflectance of a clay-soiled polyester/cotton test cloth before and after washing in the Tergotometer (Trade Mark). The reflectances were measured using a Carl Zeiss Elrepho (Trade Mark) Reflectrometer and the reflectance increase on washing (ΔR) was taken as a measure of detergency.

Examples 1 to 3

In each case a wash liquor was prepared using the ingredients stated below in the concentrations stated below, in 40°FH (ca) or 20°FH (Ca) water. The wash liquor was allowed to equilibrate for 15 minutes. Test cloth pieces (four pieces per litre, each measuring 76.2 mm × 76.2 mm) were then added and a 20-minute wash at 80°C, pH 10.0 and 55 r.p.m. agitation was carried out, followed by a rinse in water of the same hardness as that of the water used to prepare the wash liquor.

The ingredients and concentrations were as follows:

	g/litre
Sodium C_{10}—C_{13} linear alkylbenzene sulphonate	0.195
C_{14}—C_{15} alcohol ethoxylate (11 EO)	0.09
Hardeed tallow soap	0.06
Alkaline silicate	0.15
Sodium sulphate	2.00
Detergent additive according to the invention (as specified in Examples)	0.50—5.00

It will be seen that the detergent additive according to the invention was used at concentrations of from 0.50 to 5.00 g/litre, and the other components of the compositions were used at a constant total concentration of 2.495 g/litre, so that the total concentration ranged from 2.995 to 7.495 g/litre. Thus the percentage of the total composition constituted by the detergent additive of the invention at each concentration of the latter was as follows:

Concentration (of detergent additive)	Concentration (total)	% detergent additive in composition
0.50	2.995	16.70
1.50	3.995	37.55
2.00	4.495	44.49
2.50	4.995	50.05
3.00	5.495	54.60
4.00	6.495	61.59
5.00	7.495	66.71

Example 1

The detergencies of compositions containing two zeolite/precipient systems according to the invention were compared, at various concentrations, with those of compositions containing zeolite alone and compositions containing zeolite/sodium tripolyphosphate (STP), in 20°FH (Ca^{2+}) water. The organic precipitants used were disodium dodecyl malonate (C_{12}AKM) and disodium (C_{15}—C_{18}) alkyl succinate (C_{15}—C_{18} AKS); the zeolite was Zeolite A. The results were as follows:

Concentration of detergent additive	Composition of detergent additive	Reflectance (ΔR)
0.50	zeolite (100%)	10.7
	zeolite (80%)+C_{12}AKM (20%)	12.4
	zeolite (80%)+C_{15-18}AKS (20%)	11.4
	zeolite (80%)+STP (20%)	13.0
1.50	zeolite (100%)	17.1
	zeolite (80%)+C_{12}AKM (20%)	21.5
	zeolite (80%)+C_{15-18}AKS (20%)	18.4
	zeolite (80%)+STP (20%)	22.7
2.00	zeolite (100%)	20.8
	zeolite (80%)+C_{12}AKM (20%)	25.6
	zeolite (80%)+C_{15-18}AKS (20%)	24.5
	zeolite (80%)+STP (20%)	26.7
3.00	zeolite (100%)	25.6
	zeolite (80%)+C_{12}AKM (20%)	26.6
	zeolite (80%)+C_{15-18}AKS (20%)	26.0
	zeolite (80%)+STP (20%)	27.5

Example 2

The detergencies of compositions containing zeolite/disodium hexadecenyl succinate ($C_{16:1}$AKS) were compared, at various concentrations, with those of compositions containing zeolite alone and zeolite/STP in 40°FH (Ca^{2+}) water. The results were as follows:

Concentration of detergent additive	Composition of detergent additive	Reflectance (Δ R)
3.00	zeolite (100%)	16.0
	zeolite (80%) + $C_{16:1}$AKS (20%)	18.8
	zeolite (80%) + STP (20%)	21.8
4.00	zeolite (100%)	20.2
	zeolite (80%) + $C_{16:1}$AKS (20%)	25.0
	zeolite (80%) + STP (20%)	25.2
5.00	zeolite (100%)	23.2
	zeolite (80%) + $C_{16:1}$AKS (20%)	25.4
	zeolite (80%) + STP (20%)	25.7

Example 3

A detergent product was prepared from the following ingredients, the percentages being based on the total solids:

	%
Sodium C_{10}—C_{13} linear alkylbenzene sulphonate	6
C_{14}—C_{15} alcohol ethoxylate (11 EO)	3
Hardened tallow soap	5
Sodium silicate	6
Sodium sulphate	3.5
Sodium chloride	9.5
Builder (anhydrous basis)	40

The builder systems used were all-zeolite, zeolite/C_{15}—C_{18}AKS, and zeolite/hardened tallow soap. Detergencies were compared at product dosages of 3.0, 5.0 and 8.0 g/litre, in 35°H (Ca^{2+}) water at 60°C and pH 10.0, at a wash duration of 20 minutes in the Tergotometer.

The results were as follows:

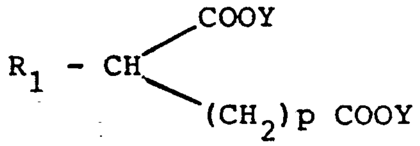
Percentage builder in product	Reflectance (ΔR) for product dosages (g/litre)		
	3.0	5.0	8.0
40% zeolite	13.0	17.5	22.2
35% zeolite+5% C_{15-18} AKS	—	19.5	23.6
35% zeolite+5% h.tallow soap	—	18.0	22.3
30% zeolite+10% C_{15-18} AKS	13.8	19.7	24.0
30% zeolite+10% h.tallow soap	12.5	18.1	22.7
25% zeolite+15% C_{15-18} AKS	14.1	20.2	24.1
25% zeolite+15% h.tallow soap	12.1	18.4	23.5

Claims

1. A detergent composition comprising from 3 to 90% by weight of one or more detergent active agents, and from 10 to 97% by weight of a builder component consisting essentially of a crystalline or amorphous aluminosilicate cation-exchange material and a supplementary precipitant builder, characterised in that the builder component consists essentially of:

(i) from 25 to 97% by weight, based on the builder component, of the aluminosilicate cation-exchange material, and

(ii) from 3% to 75% by weight of an organic precipitant builder having the formula I



$$R_1 - CH\begin{cases} COOY \\ (CH_2)p\ COOY \end{cases} \qquad (I)$$

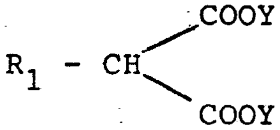
wherein:

R_1 is a C_{10}—C_{24} alkyl, alkenyl, arylalkyl or alkylaryl group;

Y is hydrogen or a solubilising cation; and

p is 0 or 1.

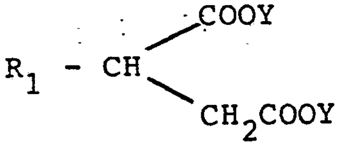
2. A detergent composition as claimed in Claim 1, characterised in that the organic precipitant builder is a compound of the formula II



$$R_1 - CH\begin{cases} COOY \\ COOY \end{cases} \qquad (II)$$

wherein R_1 and Y have the meanings given in Claim 1.

3. A detergent composition as claimed in Claim 1, characterised in that the organic precipitant builder is a compound of the formula III



$$R_1 - CH\begin{cases} COOY \\ CH_2COOY \end{cases} \qquad (III)$$

wherein R_1 and Y have the meanings given in Claim 1.

4. A detergent composition as claimed in any one of Claims 1 to 3, characterised in that the organic precipitant builder has a calcium salt solubility product of less than 10^{-8}.

5. A detergent composition as claimed in any one of Claims 1 to 4, characterised in that it contains less than 5% by weight of inorganic phosphate.

6. A detergent composition as claimed in any one of Claims 1 to 5, characterised in that it contains from 15 to 70% by weight of the detergent additive.

7. A detergent composition as claimed in any one of Claims 1 to 6, characterised in that it contains from 10 to 60% by weight of aluminosilicate cation-exchange material.

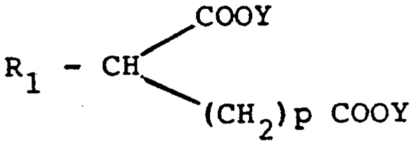
8. A detergent composition as claimed in any one of Claims 1 to 7, characterised in that it contains from 1 to 30% of the organic precipitant builder.

Patentansprüche

1. Detergenszusammensetzung, umfassend 3 bis 90 Gew.-% eines oder mehrerer reinigungsaktiver Mittel und 10 bis 97 Gew.-% einer Builderkomponente bestehend im wesentlichen aus einem kristallinen oder amorphen Aluminosilicat-Kationenaustauschmaterial und einem ergänzenden, fällenden Builder, dadurch gekennzeichnet, daß die Builderkomponente im wesentlichen besteht aus:

(i) 25 bis 97 Gew.-% des Aluminosilicat-Kationenaustauschmaterial, bezogen auf die Builderkomponente, und

(ii) 3 bis 75 Gew.-% eines organischen, fällenden Builders der Formel I



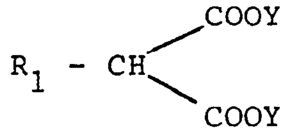
$$R_1 - CH\begin{cases} COOY \\ (CH_2)p\ COOY \end{cases} \qquad (I)$$

worin:

R_1 eine C_{10}—C_{24}-Alkyl-, Alkenyl-, Arylalkyl- oder Alkylaryl-Gruppe ist,

Y Wasserstoff oder ein löslichmachendes Kation ist und p 0 oder 1 ist.

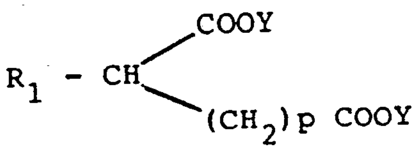
2. Detergenszusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der organische, fällende Builder eine Verbindung der Formel II



(II)

ist, worin R_1 und Y die in Anspruch 1 gegebenen Bedeutungen haben.

3. Detergenszusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der organische, fällende Builder eine Verbindung der Formel III



(III)

ist, worin R_1 und Y die in Anspruch 1 gegebenen Bedeutungen haben.

4. Detergenszusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß der organische, fällende Builder ein Calciumsalz-Lölichkeitsprodukt von weniger als 10^{-8} hat.

5. Detergenszusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß sie weniger als 5 Gew.-% anorganisches Phosphat enthält.

6. Detergenszusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß sie 15 bis 70 Gew.-% des Detergenszusatzes enthält.

7. Detergenszusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß sie 10 bis 60 Gew.-% Aluminosilicat-Kationenaustauschmaterial enthält.

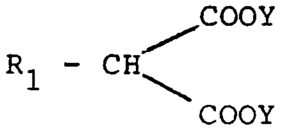
8. Detergenszusammensetzung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß sie 1 bis 30 Gew.-% des organischen, fällenden Builders enthält.

Revendications

1. Composition détergente comprenant de 3 à 90% en poids d'un ou plusieurs agents détergents actifs et de 10 à 97% en poids d'un composant adjuvant consistant essentiellement en une matière échangeuse de cations du type alumino-silicate cristallin ou amorphe et d'un précipitant-adjuvant supplémentaire, caractérisé en ce que le composant adjuvant comprend essentiellement:

(i) de 25 à 97% en poids, par rapport au composant adjuvant, d'un alumino-silicate échangeur de cations; et

(ii) de 3 à 75% en poids d'un précipitant-adjuvant organique de formule



(II)

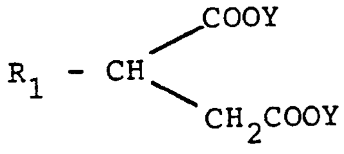
dans laquelle:

R_1 est un radical alkyle en C_{10}—C_{24}, alcényle, arylalkyle ou alkylaryle;

Y est un atome d'hydrogène ou un cation solubilisant;

p est 0 ou 1.

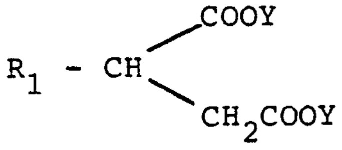
2. Composition détergente selon la revendication 1, caractérisée en ce que le précipitant adjuvant organique est un composé de formule II



(III)

dans laquelle R_1 et Y ont les mêmes significations que dans la revendication 1.

3. Composition détergente selon la revendication 1, caractérisée en ce que le précipitant adjuvant organique est un composé de formule III



$$R_1 - CH\begin{matrix} \diagup COOY \\ \diagdown CH_2COOY \end{matrix} \qquad (III)$$

dans laquelle R_1 et Y ont les mêmes significations que dans la revendication 1.

4. Composition détergente selon l'une quelconque des revendications 1 à 3, caractérisée en ce que le précipitant adjuvant organique a un produit de solubilité de sel de calcium de moins de 10^{-8}.

5. Composition détergente selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle contient moins de 5% en poids de phosphate minéral.

6. Composition détergente selon l'une quelconque des revendications 1 à 5, caractérisée en ce qu'elle contient de 15 à 70% en poids de l'additif au détergent.

7. Composition détergente selon l'une quelconque des revendications 1 à 6, caractérisée en ce qu'elle contient de 10 à 60% en poids d'alumino-silicate échangeur de cations.

8. Composition détergente selon l'une quelconque des revendications 1 à 7, caractérisée en ce qu'elle contient de 1 à 30% de précipitant adjuvant organique.