⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 070 190**
A1

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: 82303674.4

㉒ Date of filing: 13.07.82

(51) Int. Cl.^{3}: **C 11 D 3/12**

㉚ Priority: 15.07.81 GB 8121837

㊸ Date of publication of application:
19.01.83 Bulletin 83/3

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(71) Applicant: UNILEVER PLC
Unilever House Blackfriars P O Box 68
London EC4P 4BQ(GB)

(84) Designated Contracting States:
GB

(71) Applicant: UNILEVER NV
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

(84) Designated Contracting States:
BE CH DE FR IT LI NL SE AT

(72) Inventor: Scowen, Reginald Vear
113 Brookhurst Road
Bromborough Wirral Merseyside(GB)

(72) Inventor: Stirling, Thomas
78 Davenham Avenue
Oxton Birkenhead Merseyside(GB)

(72) Inventor: Welch, Gordon Joseph
53 Thackeray Drive
Vickers Cross Chester(GB)

(74) Representative: Fransella, Mary Evelyn et al,
Unilever PLC Patent Division P.O. Box 31 Salisbury
Square House Salisbury Square
London EC4P 4AN(GB)

(54) Detergent additives and detergent compositions containing them.

(57) A builder system for detergent compositions comprises 25 to 97% by weight of an aluminosilicate cation-exchange material such as Zeolite A and 3 to 75% by weight, in total, of an organic precipitant builder having a polyvalent anion, for example, an alkyl or alkenyl malonate or succinate, and an organic sequestrant such as a nitrilotriacetate. The ratio of precipitant to sequestrant is 10:1 to 1:10. The builder mix is advantageously used in detergent compositions containing less than 10% inorganic phosphate, and gives good results in zero-phosphate compositions.

DETERGENT ADDITIVES AND DETERGENT COMPOSITIONS CONTAINING THEM

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 efficient 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 or environmental reasons.

We have now discovered that surprisingly good detergency results are obtained by using, in combination with an aluminosilicate builder, relatively small amounts of both an organic sequestrant builder and of an organic precipitant builder. The detergency results obtained using ternary systems of this type have surprisingly been found to be better than would have been expected from consideration of the results obtained using the corresponding binary aluminosilicate/sequestrant and aluminosilicate/precipitant systems, so that decreased amounts of the supplementary builders can be used, giving cost savings and environmental advantages.

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., <u>55</u> , 52-53 (1978). The complexing agent is able to take up polvalent water hardness ions (notably 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 magnesium salt).

It is thus unexpected that addition of a precipitant builder and an aluminosilicate/sequestrant system gives a substantial improvement in detergency builder properties.

The present invention accordingly provides, in a first aspect, a detergent additive consisting essentially of:

(a) from about 25% to about 97% by weight of a crystalline or amorphous aluminosilicate cation-exchange material,
(b) from about 3% to about 75% by weight, in total, of
  (i) an organic precipitant builder having a polyvalent anion, which builder forms an insoluble calcium salt, and
  (ii) an organic builder which forms a soluble complex with calcium,

the weight ratio of (i) to (ii) being from about 10:1 to about 1:10.

The organic precipitant builder is preferably one having a divalent anion.

The aluminosilicate cation exchange material is a 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 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:

$$Na_2O.Al_2O_3.2SiO_2.\sim 4.5H_2O$$

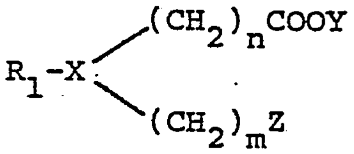
and is also described by the unit cell content:

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

The organic precipitant builder is a water-soluble material which forms an insoluble calcium salt and which has a polyvalent, preferably divalent, anion. Materials having a divalent anion are substantially more weight-effective as builders than are soaps; only one mole is consumed by each gram ion of Ca^{2+} or Mg^{2+} hardness ions, as compared with two moles of soap.

The solubility product of the calcium salt of the organic precipitant builder having a divalent anion is preferably less than 10^{-8}.

Advantageously the organic precipitant builder is a compound of the formula I:



$$R_1{-}X\left\langle\begin{array}{l}(CH_2)_nCOOY\\ \\(CH_2)_mZ\end{array}\right. \qquad \text{(I)}$$

wherein:

R_1 is C_{10}-C_{24} alkyl or alkenyl, or an arylalkyl or alkylaryl group of equivalent chain length;

X is CH, CR_2, N or CON;

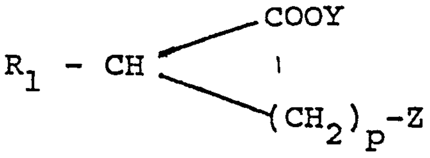
R_2 is C_1-C_3 alkyl;

Y is hydrogen or a solubilising cation, preferably alkali metal and especially sodium;

n and m, which may be the same or different, are 0 or integers from 1 to 4; and

Z is COOY or SO_3Y.

One preferred group of compounds within this definition consists of those in which X is CH, n is zero, and m is 0 or 1. Thus, according to a first preferred embodiment of the invention, the organic precipitant builder is a compound of the formula II.

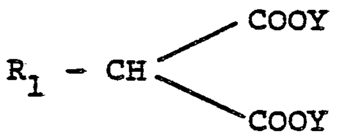


$$R_1 - CH\left\langle\begin{array}{l}COOY\\ \\(CH_2)_p{-}Z\end{array}\right. \qquad \text{(II)}$$

wherein R_1, Y and Z have the meanings given above, and p is 0 or 1.

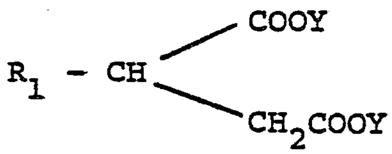
Especially preferred classes of compounds within the general formula II are the following:

(i) substituted malonates of the formula III:



$$\mathrm{R_1-CH}\left\langle\begin{array}{l}\mathrm{COOY}\\ \mathrm{COOY}\end{array}\right.\qquad \mathrm{(III)}$$

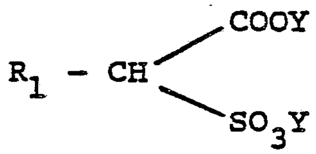
(ii) substituted succinates of the formula IV:



$$\mathrm{R_1-CH}\left\langle\begin{array}{l}\mathrm{COOY}\\ \mathrm{CH_2COOY}\end{array}\right.\qquad \mathrm{(IV)}$$

- and -

(iii) α-sulphofatty acid salts of the formula V:

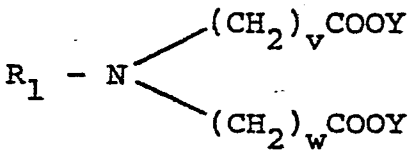


$$\mathrm{R_1-CH}\left\langle\begin{array}{l}\mathrm{COOY}\\ \mathrm{SO_3Y}\end{array}\right.\qquad \mathrm{(V)}$$

Compounds of the formulae III and IV 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).

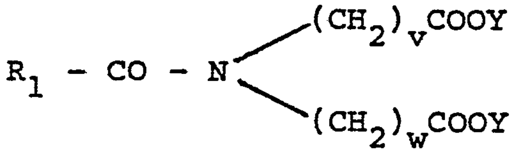
Compounds of the formula V are described, for example, in GB 1,368,736 and GB 1,380,390 (Unilever). A typical example is disodium α-sulphostearate (C_{18}-SFAS). Blends of compounds of different chain lengths, for example the α-sulpho salt of coconut fatty acids (coco-SFAS), or of tallow fatty acids (tallow-SFAS), or of blended coconut and tallow fatty acids, may also advantageously be used.

According to a second preferred embodiment of the invention, the organic precipitant builder is a compound of the formula VI:



$$R_1 - N\Big\langle\begin{matrix}(CH_2)_v COOY\\ (CH_2)_w COOY\end{matrix} \qquad (VI)$$

or of the formula VII:



$$R_1 - CO - N\Big\langle\begin{matrix}(CH_2)_v COOY\\ (CH_2)_w COOY\end{matrix} \qquad (VII)$$

wherein R_1 and Y have the meanings given above and v and w are each 1 to 4, preferably 1 or 2.

Compounds of the formula VI in which v and w are both 1, the N-alkyl iminodiacetates, are of especial interest.

Compounds of the formula VI in which v and w are both 2, the β-iminodipropionates, are known amphoteric surfactants, disclosed, for example, in GB 1,296,793 (General Mills). These materials are also known as lather promoters in soap bars, a for example, in EP 0 025 242 (Procter & Gamble), and as anti-corrosive agents, for example, in US 2,926,108 (General Mills). Compounds of the formula VI in which v and w are both 1, the iminodiacetates, have also been disclosed, for example, as scum dispersants in soap products, in US 3,630,927 (Monsanto), and as anti-corrosive agents, in US 2,368,604 (Shell). US 3,981,779 (Grace) discloses compounds of both formulae VI and VII for use as "chelant-surfactants" for decreasing the fouling of metals by aqueous systems.

GB 761,384 (California Research Corporation) discloses detergent compositions containing 10 to 50% by weight of alkylbenzene sulphonate and 5 to 20% by weight of a water-soluble salt of an N-(C_8-C_{18} alkyl)-iminodiacetic acid, the latter component acting as a foam promoter. Similarly, GB 761,383 (California Research Corporation) discloses combinations of alkyl sulphates and N-(C_8-C_{18} alkyl)-iminodicarboxylic acids. Other specifications relating to the use of compounds of the formula VI in detergent compositions are GB 446,737 and GB 446,813 (I G Farben). Compounds analogous to those of formula VI but having a shorter alkyl chain (C_8 or less) are known as sequestrant builders, as in GB 1,383,025 (Chemische Werke Hüls), and as rancidity preventers in soaps and non-soap detergents, as in GB 574,504 (Unilever).

The organic sequestrant builder is a water-soluble material which forms soluble complexes with calcium, preferably with pK_{Ca} greater than 3.0, preferably greater than 4.0 and more preferably greater than 4.5. Advantageously the sequestrant builder also forms complexes with magnesium, preferably with pK_{Mg} greater than 4.0.

Examples of suitable materials include alkali metal (especially sodium) salts of the following acids: nitrilotriacetic acid, ethylenediamine tetracetic acid, polyacrylic acid, poly(-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.

Alkali metal salts of nitrilotriacetic acid (NTA), especially the trisodium salt, are, however, the preferred organic sequestrants used according to the present invention. The use of NTA salts in combination with precipitant builders having a divalent anion is especially preferred.

The nitrilotriacetic acid compounds preferably used according to the present invention are known sequestering agents and may be represented by the following structural formula

$$N{=\!=}(CH_2COOX)_3$$

wherein X, as before is hydrogen or a solubilizing cation. These compounds further contain C-bonded substituents of an inert and innoxious nature such as alkyl, eg methyl or ethyl, or haloalkyl, eg chloromethyl. The nature of said compounds is not particularly critical with the implicit limitation that such substituents be devoid of any tendency to deleteriously affect the desirable properties of the nitrilotriacetic acid compound.

Preferred compounds falling within the ambit of the above-described definition and formula are nitrilotriacetic acid, trisodium nitrilotriacetate monohydrate, tripotassium nitrilotriacetate, disodium nitrilotriacetate and dipotassium nitrilotriacetate.

The organic precipitant builder and the organic sequestrant builder together constitute from about 3% to about 75% by weight of the builder mix (detergent additive) of the invention, preferably from about 10% to about 60% and especially from about 20% to about 50%. The ratio of precipitant to sequestrant is from 10:1 to 1:10, preferably from 3:1 to 1:3 and desirably from 3:1 to 1:1.

The detergent additive of the present invention is an efficient builder system yielding good detergency results when incorporated, with detergent-active materials, in a detergent composition.

Accordingly, in a second aspect the present invention provides a detergent composition comprising from about 3 to about 90% by weight of at least one synthetic detergent-active material, and from about 10 to about 97% by weight of a detergent additive as previously defined.

The detergent composition of the invention contains from about 10% to about 97% by weight of the detergent additive of the invention, preferably from about 10% to about 80%. more preferably from about 25% to about 70%, and especially from about 28% to about 67%.

Since the detergent additive contains from about 25% to about 97% by weight of aluminosilicate, the aluminosilicate content of the detergent composition can range from about 2.5% to about 94%. An aluminosilicate content of from about 10% to about 60%, especially from about 17% to about 47%, is preferred.

Similarly, the content of organic builders (precipitant plus sequestrant) can range from about 0.3% to about 73%, a range of from about 5% to about 40%. especially from about 7% to about 27%, being preferred. The preferred range for the content of the precipitant builder is from about 3% to about 20%, especially from about 5% to about 10%; for the sequestrant builder the preferred range is from about 1% to about 15%, especially from about 2% to about 10%.

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; a level below 5% is advantageous, and a level below 3% is especially preferred. Any phosphate present may, for example, be in the form of alkali metal (preferably sodium) tripolyphosphate, orthophosphate, pyrophosphate or polymeric phosphate.

The detergent composition of the invention necessarily includes from about 3% to about 90% by weight, preferably from about 5% to about 40% by weight, more preferably from about 10% to about 25% by weight, of a synthetic anionic, nonionic, amphoteric or zwitterionic detergent compound or mixture 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 sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced for example from tallow or coconut oil; sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, 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, ie 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 this 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, ie 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 peroxybleach 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-acetoxy-(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-dimetyl-2,5-diketopiperazine;

(l) Acylation products of propylenediurea or 2,2-dimethyl-propylenediurea (2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonane-3,7-dione or its 9,9-dimethyl derivative), especially the tetraacetyl- or the tetrapropionyl-propylenediurea or their dimethyl derivatives;

(m) Carbonic acid esters, for example the sodium salts of p-(ethoxycarbonyloxy)-benzoic acid and p-(propoxy-carbonyloxy)-benzenesulphonic acid.

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

The N-diacylated and N,N'-polyacylatedamines 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 our UK Patent Application No. 80 21979. 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 applied. 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 particularly 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 salt form, especially in calcium, magnesium, zinc or aluminium salt form, as described in our UK Patent Application No. 2 048 930.

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 meta-silicates 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 acidic 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 washing 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. The reflectances were measured using a Carl Zeiss Elrepho Reflectometer and the reflectance increase on washing (ΔR) was taken as a measure of detergency.

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 x 76.2 mm) were then added and a 20-minute wash at 80°C, pH 10.0 and 55 rpm 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
Hardened tallow soap	0.06
Alkaline silicate	0.15

	g/litre
Sodium sulphate	2.00
Detergent additive according to the invention (as specified in Examples)	1.00-5.00

It will be seen that the detergent additive according to the invention was used at concentrations of from 1.00 to 5.00 g/litre, and the other components of the composition were used at a constant total concentration of 2.495 g/litre, so that the total concentration ranged from 3.495 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		% detergent additive in composition
(of detergent additive)	(total)	
1.00	3.495	28.61
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

All percentages given in the Examples are by weight and are based on the anhydrous materials.

EXAMPLE 1

The detergencies of compositions containing a ternary builder system (detergent additive) according to the invention were compared at two different concentrations and water hardnesses, with those of control compositions containing single or binary builder systems. The aluminosilicate used was zeolite A, the organic precipitant was disodium dodecylmalonate (C_{12}AKM), and the organic sequestrant was trisodium nitrilotriacetate (NTA). The results were as follows:

	Reflectance ΔR			
	In 20°FH Ca water		In 40°FH Ca water	
Concentration, g/l	1.0	1.5	2.5	4.0
Detergent additive				
60% zeolite/25% C_{12} AKM/15% NTA	22.6	26.0	25.4	28.5
85% zeolite 15%/NTA	18.5	24.5	20.1	26.7
75% zeolite/25% C_{12} AKM	17.4	24.0	21.2	25.8
100% zeolite	16.4	20.8	16.5	25.0

EXAMPLE 2

A similar procedure to that of Example 1 was carried out using the organic sequestrant trisodium carboxymethyloxysuccinate (CMOS) instead of NTA. The results were as follows:

	Reflectance ΔR			
	In 20°FH Ca water		In 40°FH Ca water	
Concentration, g/l	1.0	2.0	4.0	5.0
Detergent additive				
60% zeolite/25% C_{12} AKM/15% CMOS	18.5	26.9	26.5	27.0
85% zeolite/15% CMOS	16.8	23.5	24.1	24.7
75% zeolite/25% C_{12}AKM	17.4	26.1	25.8	26.6
100% zeolite	16.4	25.1	25.0	25.8

EXAMPLE 3

A similar procedure to that of Example 1 was carried out using the organic sequestrant poly (α-hydroxy acrylate) (PHAC) instead of NTA. The tests at 2.5 g/l and in 40° FH (Ca^{2+}) water were carried out using a different test cloth, one with a predominantly fatty soil. The results were as follows:

	Reflectance ΔR	
	In 40°FH Ca water (fatty test cloth)	In 40°FH Ca water (clay-soiled test cloth)
Concentration, g/l	2.5	3.0
Detergent additive		
60% zeolite/25% C_{12} AKM/15% PHAC	29.1	28.0
85% zeolite/15% PHAC	28.1	25.6
75% zeolite/25% C_{12} AKM	28.0	24.1
100% zeolite	26.6	19.8

EXAMPLE 4

A similar procedure to that of Example 1 was carried out using as organic sequestrant a polyacrylate (Versicol E7) instead of NTA. The tests were carried out at 3.0 g/l and in 40°FH (Ca^{2+}) water, and the results were as follows:

Detergent additive	Reflectance ΔR
60% zeolite/25% C_{12} AKM/15% polyacrylate	25.3
85% zeolite/15% polyacrylate	22.0

Detergent additive	Reflectance ΔR
75% zeolite/25% C_{12} AKM	24.1
100% zeolite	19.8

EXAMPLE 5

A similar procedure to that of Example 1 was carried out using as organic sequestrant tetrasodium ethylenediamine-tetraacetate (EDTA) instead of NTA, at 3.0 g/l and in 40° FH (Ca^{2+}) water. The results were as follows:

Detergent additive	Reflectance ΔR
60% zeolite/25% C_{12} AKM/15% EDTA	26.3
85% zeolite/15% EDTA	22.6
75% zeolite/25% C_{12} AKM	24.1
100% zeolite	19.8

EXAMPLE 6

A similar procedure to that of Example 1 was carried out using as organic sequestrant tetrasodium oxydisuccinate (ODS) instead of NTA, at 3.0 g/l and in 40° FH (Ca^{2+}) water. The results were as follows:

Detergent additive	Reflectance ΔR
60% zeolite/25% C_{12} AKM/15% ODS	24.9
85% zeolite/15% ODS	23.4
75% zeolite/25% C_{12} AKM	24.1
100% zeolite	19.8

EXAMPLE 7

A similar procedure to that of Example 1 was carried out using as organic sequestrant instead of NTA, an oxidised starch as described in GB 1,330,121. The tests were carried out at 3.0 g/l in 40° FH (Ca^{2+}) water and the results were as follows:

Detergent additive	Reflectance ΔR
60% zeolite/25% C_{12} AKM/15% oxidised starch	25.2
85% zeolite/15% oxidised starch	21.1
75% zeolite/25% C_{12} AKM	24.1
100% zeolite	19.8

EXAMPLE 8

A similar procedure to that of Example 1 was carried out using as organic precipitant, instead of C_{12} AKM, disodium hexadecenyl succinate (C_{16} AKS). The tests were carried out in 40° FH (Ca^{2+}) water and the results were as follows:

	Reflectance ΔR		
Concentration, g/l	2.0	2.5	4.0
Detergent additive			
60% zeolite/25% C_{16} AKS/15% NTA	19.5	25.9	27.2
85% zeolite/15% NTA	15.9	21.2	25.0
75% zeolite/25% C_{16} AKS	16.2	20.3	24.5
100% zeolite	14.6	17.3	23.0

EXAMPLE 9

A similar procedure to that of Example 1 was carried out using, as organic precipitant, instead of C_{12} AKM, disodium α-sulphostearate (C_{18} SFAS). The tests were carried out in 40° FH (Ca^{2+}) water and the results were as follows:

	Reflectance ΔR		
Concentration, g/l	2.5	3.0	4.0
Detergent additive			
60% zeolite/25% C_{18} SFAS/15% NTA	22.7	24.8	27.1
85% zeolite/15% NTA	21.2	23.5	25.0
75% zeolite/25% C_{18} SFAS	19.6	21.5	23.4
100% zeolite	17.2	19.5	23.0

EXAMPLE 10

A similar procedure to that of Example 1 was carried out using, as organic precipitant, instead of C_{12}AKM, disodium hexadecyliminodiacetate (C_{16}IMA). The tests were carried out at a total builder concentration of 4 g/litre in 40°FH (Ca^{2+}) water. Tests were carried out using both a clay-soiled test cloth and a test cloth soiled with a mixture of organic and particulate soils. The results were as follows:

Detergent additive	Reflectance (Δ R) Clay-soiled test cloth	Reflectance (Δ R) Mixed-soil test cloth
100% zeolite	14.0	31.5
90% zeolite/10% NTA	16.5	32.9
80% zeolite/20% C_{16}IMA	13.6	31.1
70% zeolite/20% C_{16}IMA/ 10% NTA	17.3	33.5
70% zeolite/30% C_{16}IMA	15.0	not tested
60% zeolite/30% C_{16}IMA/ 10% NTA	18.0	not tested
80% zeolite/20% STP	17.4	34.1

CLAIMS

1. A detergent additive characterised in that it consists essentially of:

(a) from 25% to 97% by weight of a crystalline or amorphous aluminosilicate cation-exchange material,

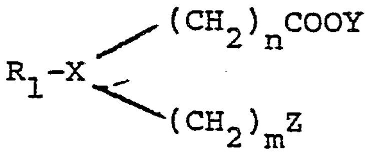
(b) from 3% to 75% by weight, in total, of

- (i) an organic precipitant builder having a polyvalent anion, which builder forms an insoluble calcium salt, and
- (ii) an organic sequestrant builder which forms a soluble complex with calcium,

the weight ratio of (i) to (ii) being from 10:1 to 1:10.

2. A detergent additive as claimed in Claim 1, characterised in that the organic precipitant builder has a divalent anion.

3. A detergent additive as claimed in Claim 2, characterised in that the organic precipitant builder is a compound of the formula I



$$R_1{-}X\begin{cases}(CH_2)_nCOOY\\(CH_2)_mZ\end{cases}\qquad (I)$$

wherein

R_1 is C_{10}-C_{24} alkyl or alkenyl, or an arylalkyl or alkylaryl group of equivalent chain length;

X is CH, CR_2, N or CON;

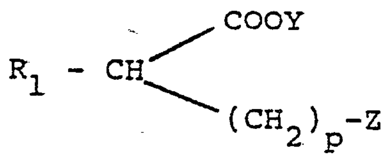
R_2 is C_1-C_3 alkyl;

Y is hydrogen or a solubilising cation;

<u>n</u> and <u>m</u>, which may be the same or different, are 0 or integers from 1 to 4; and

Z is COOY or SO_3Y.

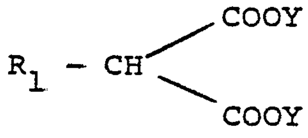
4. A detergent additive as claimed in Claim 3, characterised in that the organic precipitant builder is a compound of the formula II



$$R_1 - CH\begin{cases}COOY\\(CH_2)_p-Z\end{cases} \tag{II}$$

wherein R_1, Y and Z have the meanings given in Claim 3, and p is 0 or 1.

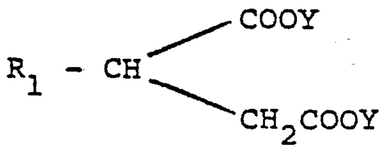
5. A detergent additive as claimed in Claim 4, characterised in that the the organic precipitant builder is a compound of the formula III



$$R_1 - CH\begin{cases}COOY\\COOY\end{cases} \tag{III}$$

wherein R_1 and Y have the meanings given in Claim 3.

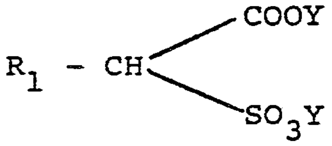
6. A detergent additive as claimed in Claim 4, characterised in that the organic precipitant builder is a compound of the formula IV



$$R_1 - CH\begin{cases}COOY\\CH_2COOY\end{cases} \tag{IV}$$

wherein R_1 and Y have the meanings given in Claim 3.

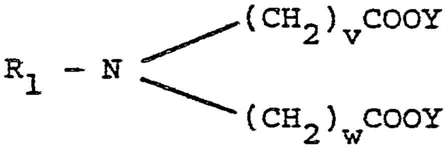
7. A detergent additive as claimed in Claim 4, characterised in that the organic precipitant builder is a compound of the formula V


(V)

$$R_1 - CH \begin{cases} COOY \\ SO_3Y \end{cases}$$

wherein R_1 and Y have the meanings given in Claim 3.

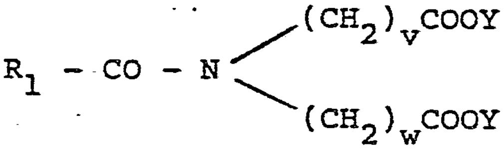
8. A detergent additive as claimed in Claim 3, characterised in that the organic precipitant builder is a compound of the formula VI


(VI)

$$R_1 - N \begin{cases} (CH_2)_vCOOY \\ (CH_2)_wCOOY \end{cases}$$

wherein R_1 and Y have the meanings given in Claim 3, and v and w are each integers within the range of from 1 to 4.

9. A detergent additive as claimed in Claim 3, characterised in that the organic precipitant builder is a compound of the formula VII


(VII)

$$R_1 - CO - N \begin{cases} (CH_2)_vCOOY \\ (CH_2)_wCOOY \end{cases}$$

wherein R_1 and Y have the meanings given in Claim 3, and v and w are each integers withih the range of from 1 to 4.

10. A detergent additive as claimed in any one of Claims 1 to 9, characterised in that the organic sequestrant builder is an alkali metal salt of an organic carboxylic acid having three or more carboxyl groups.

11. A detergent additive as claimed in Claim 10, characterised in that the organic sequestrant builder is an alkali metal salt of nitrilotriacetic acid.

12. A detergent additive as claimed in Claim 10, characterised in that the organic sequestrant builder is selected from alkali metal salts of ethylenediaminetetraacetic acid, polyacrylic acid, poly(-hydroxyacrylic) acid, carboxymethyloxymalonic acid, carboxymethyloxysuccinic acid, oxydiacetic acid, oxydisuccinic acid, citric acid, dipicolinic acid, polyacetal carboxylates and oxidised polysaccharides.

13. A detergent additive as claimed in any one of Claims 1 to 12, characterised in that the aluminosilicate cation exchange material is a crystalline material having a unit cell of the formula IX

$$Na_x\,(AlO_2)_x\cdot(SiO_2)_y\;zH_2O \qquad (IX)$$

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.

14. A detergent additive as claimed in Claim 13, characterised in that the aluminosilicate cation exchange material is a crystalline material having a unit cell of the formula X

$$Na_{12}(AlO_2)_{12}\cdot(SiO_2)_{12}\cdot zH_2O \qquad X$$

wherein z is from 20 to 30.

15. A detergent additive as claimed in any one of Claims 1 to 14, characterised in that it contains from 10 to 60% by weight, in total, of the organic precipitant builder and the organic sequestrant builder.

16. A detergent additive as claimed in any one of Claims 1 to 15, characterised in that the weight ratio of the organic precipitant builder to the organic sequestrant builder is from 3:1 to 1:3.

17. A detergent composition which comprises from 3 to 90% by weight of at least one synthetic detergent-active material and from 10 to 97% by weight of a detergent additive as claimed in any one of Claims 1 to 16.

18. A detergent composition as claimed in Claim 17, characterised in that it contains less than 5% by weight of inorganic phosphate.

European Patent
Office

EUROPEAN SEARCH REPORT

Application number
EP 82 30 3674.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	DE - A1 - 2 525 778 (PROCTER & GAMBLE CO.) * claims 1, 5, 6, 11, 12, 15 * & GB - A - 1 501 498 --	1, 10-14	C 11 D 3/12
Y	DE - A - 2 422 655 (PROCTER & GAMBLE CO.) * claims 1, 3 to 6, 13 * --	1, 10-14	
A	DE - A1 - 2 843 709 (PQ-CORP.) * claims 1, 3, 7, 10 * & GB - A - 2 006 257 ----		

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	31-08-1982	SCHULTZE