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(54) Detergent compositions.

(57) A particulate alkaline detergent with unexpectantly good bleaching performance and with reduced phosphorus content contains 5-40% detergent active, 12.5-25% tripolyphosphate, 7.0-36% aluminosilicate builder such as zeolite, 5-30% peroxybleach such as sodium perborate and 0.1 to 15% activator such as TAED, the perborate to TAED ratio being between 2:1 and 15:1. The detergent active may be anionic material or a mixture of an anionic material and a minor amount of nonionic material. The compositions are particularly suitable for containing fluorescers and show surprisingly improved bleaching performance as water hardness increases.

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DETERGENT COMPOSITIONS

This invention relates to detergent compositions which are particularly, but not essentially, adapted for fabric washing, and more particularly to phosphate built detergent compositions including a bleach system.

It is known to incorporate peracid bleaches such as sodium perborate, together with peracid bleach precursors or peroxy bleach activator in detergent compositions. Such detergent compositions conventionally include, in addition to a detergent active material, a phosphate detergency builder 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 in detergent compositions.

Water-insoluble alumino-silicate ion exchange materials have been suggested as alternative builders to phosphates. (See for example GB 1 429 143 - Procter & Gamble Co.) However, it has been found that in alumino-silicate built compositions the performance of this bleach system is significantly reduced.

It has also been found that, where a detergent composition is based on aluminosilicate as the only builder, or on sodium tripolyphosphate as the only builder, the bleach performance of the composition is reduced as the final water hardness is increased. Thus, for a fixed product dosage where the level of builder material in the product is intentionally reduced, possibly as a cost saving exercise, or where the product is used at a dosage which is lower than that recommended, the bleach performance of the product is reduced.

We have now surprisingly found however, that the bleach performance can be substantially maintained and that the reduction in bleach performance with increasing water hardness can be substantially overcome if only a specific part of the tripolyphosphate is replaced by the alumino-silicate and if the peroxy bleach and the activator therefor are present in specific relative proportions.

Thus, according to the invention there is provided a particulate alkaline detergent composition comprising:

from about 5% to about 40% by weight of at least one synthetic detergent active material;

from about 12.5% to about 25% by weight of an alkali metal tripolyphosphate calculated on an anhydrous basis;

from about 7.0% to about 36% by weight of a water-insoluble aluminosilicate detergency builder material calculated on an anhydrous basis;

from about 5% to about 30% by weight of a peroxy bleach; and

up to about 15% by weight of an activator for said peroxy bleach,

the weight ratio of said peroxy bleach to said activator being between about 2:1 and about 15:1.

It is particularly beneficial if the percentage quantity of alkali metal tripolyphosphate (T) and the percentage quantity of the aluminosilicate material (A) are related to each other in such a manner that the sum

$$T + 0.5\,A$$

lies between about 25 and about 37, preferably between about 28 and about 34.

The detergent compositions of the invention necessarily include from about 5% to about 40%, preferably 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.

Generally, fabric washing detergent compositions also contain fluorescent agents for improving the brightening activity of the compositions towards fabrics washed therewith. The fluorescent agents commonly used are derivatives of 4,4'-di(sym-triazinylamino)-stilbene-2,2'-disulphonic acid or salts thereof. Other fluorescent agents that have also been used for example are derivatives of diphenyldistryryl compounds, such as 4,4'-di(3-sulphostyryl)-diphenyl; derivatives of 4,4'-di(triazolyl)-stilbene-2,2'-disulphonic acid and derivatives of diphenyl-^{2}-pyrazoline. Such fluorescent agents, however, when incorporated in bleaching detergent compositions are liable to decompose with consequent loss of fluorescent activity, possibly owing to interaction with the bleaching system therein.

We have now surprisingly found that the fluorescer stability can be substantially maintained if a major part of the detergent active material is constituted by an anionic material. Thus, it is preferred that the detergent active material selected from anionic synthetic detergent active materials and mixtures thereof with a lesser amount of one or more non-anionic synthetic detergent active materials.

The synthetic anionic detergent compounds 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 bisulphite 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, preferably together with the anionic detergent compounds 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 oxides 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 the anionic detergent compounds with, for example, nonionic compounds may be used in the detergent compositions, particularly to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic washing machines. The presence of some nonionic detergent compounds in the compositions may also help to improve the solubility characteristics of the detergent powder. A preferred anionic to nonionic ratio is at least about 2:1, most preferably from about 3:1 to about 10:1.

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 nonionic detergent compounds.

Some soaps may also be used in the compositions of the invention, but not as the sole detergent compounds. They are particularly useful at low levels in binary (soap/anionic) or ternary mixtures together with nonionic or mixed synthetic anionic and nonionic detergent compounds, which have low sudsing properties. The soaps which are used are preferably the sodium, or less desirably potassium, salts of C_{10}-C_{24} fatty acids. It is particularly preferred that the soaps should be based mainly on the longer-chain fatty acids within this range, that is with at least half of the soap having a carbon chain length of 16 or over. This is most conveniently accomplished by using soaps from natural sources such as tallow, palm oil or rapeseed oil, which can be hardened if desired, with lesser amounts of other shorter-chain soaps, prepared from nut oils such as coconut oil or palm kernel oil. The amount of such soaps can be varied between about 0.5% and about 25% by weight, with lower amounts of about

0.5% to about 5% being generally sufficient for lather control. Amounts of soap between about 2% and about 20%, especially between about 5% and about 15%, are preferably used to give a beneficial effect on detergency. This is particularly valuable in compositions used in hard water when the soap acts as a supplementary builder. In addition, we have found that the addition of soap helps to decrease the tendency of the compositions to form inorganic deposits in the wash, for which purpose it is preferred to use about 2% to about 15%, especially about 2.5% to about 10% by weight of soap in the composition. When soap is present, it is preferred that the total level of detergent actives, including the soap, lies between about 5% and about 40% by weight, most preferably between about 10% and about 25% by weight. Further, when both the soap and a nonionic detergent active material are present together with a synthetic anionic detergent active material, it is preferred that the weight ratio of the synthetic anionic material and soap to the nonionic material is at least about 2:1, most preferably about 3:1 to about 10:1.

The alkali tripolyphosphate is preferably sodium tripolyphosphate, advantageously present in an amount of from more than about 15% to about 22% by weight. While it is desirable that the only phosphate material present is the tripolyphosphate, up to about 5% by weight of the composition of other phosphate materials may also be added, such as orthophosphate or pyrophosphate. Low levels of these other phosphate materials , even over 5% by weight of the composition, may in any case be present in compositions which have been prepared by spray drying, as a consequence of the hydrolysis of sodium tripolypohosphate. Thus, for example, a spray dried product nominally containing 25% sodium tripolyphosphate (STP) may in fact contain up to about 10% by weight of other phosphates derived from the breakdown of the tripolyphosphate. The resulting sodium orthophosphate and sodium pyrophosphate both contribute to fabric ashing and should be kept to a minimum.

Although careful control of processing conditions can reduce this STP breakdown, it is preferred to prevent all breakdown in the spray drying tower by post dosing all the STP. There may still be some ortho- and pyrophosphate in the final powder because the raw material STP may contain about 5% of them and some further breakdown may occur during storage.

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

$$Na_Z \ (AlO_2)_Z \ (SiO_2)_Y \quad x \ H_2O$$

wherein Z and Y are integers of at least 6, the molar ratio of Z to Y is in the range from 1.0 to 0.5, and x is an integer from 15 to 264 such that the moisture content is from 10% to 28% by weight. The preferred range of aluminosilicate is from about 12% to about 30% on an anhydrous basis. The alumino-silicate preferably has a particle size of from 0.1 to 100 microns, ideally between 0.1 and 10 microns and a calcium ion exchange capacity of at least 200 mg.calcium carbonate/g. In a preferred embodiment, the water-insoluble aluminosilicate ion exchange material has the formula

$$Na_{12}(AlO_2SiO_2)_{12}xH_2O$$

wherein x is an integer of from 20 to 30, preferably about 27. This material is available commercially as Zeolite A.

The bleach system used essentially comprises a peroxy bleach compound which is an inorganic persalt, and an activator therefor. 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 such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the activator therefor 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 the peroxybleach compound. The ratio by weight of the peroxy bleach compound to the activator is about 15:1 to about 2:1, preferably about 10:1 to about 3.5:1. Whilst the amount of the bleach system, i.e. peroxy bleach compound and activator may be varied between about 5% and about 35% by weight of the detergent compositions, it is preferred to use about 6% to about 30% of the ingredients forming the bleach system. Thus, the preferred level of the peroxy bleach compound in the composition is between about 5.5% and about 27% by weight, while the preferred level of the activator is between about 0.5% and about 10%, most preferably between about 0.5% and about 3.2% by weight.

Typical examples of suitable peroxybleach compounds are alkalimetal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persilicates and perphosphates, of which sodium perborate is preferred. The peroxybleach compound is normally added in separately to the detergent base powder, and it is desirable to avoid segregation by having the particles of both of generally the same order.

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-(NN,N')-polyacylmalonamide, for exampleα-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 anydride, 4-chloro phthalic anhydride;

(h) Sugar esters, for example glycose 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-(propoxycarbonyloxy)-benzenesulphonic acid.

(n) Acyloxy-(N,N^1)polyacyl malonamides, such as α-acetoxy(N,N^1)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. 8021979 Specifically, it is preferred to have an activator of an average particle size of less than 150 micrometers, 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 greater than 300 µm, and not more than 20% by weight of particles greater than 200 µm, preferably greater than 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 greater than 1700 µm and up to 10% by weight of granules less than 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 tripolyphospate 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 activators can be used in acid or salts form, especially in calcium, magnesium, zinc or aluminium salt form, as described in our UK patent application 7,912,141. The stabiliser may be present at a level of up to about 1% by weight, preferably between about 0.1% and about 0.5% by weight.

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 and silicates, anti-redeposition agents such as sodium carboxymethylcellulose and alkyl or substituted alkyl cellulose ethers other stabilisers such as ethylenediamine tetraacetic acid, 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, germicides and colourants. In particular, compositions according to the invention may include the salt of an alkyl phosphoric acid as suds-suppressant and a wax as hydrophobic material as disclosed in DOS 2 701 664.

The fluorescent agents which can be used in the bleaching detergent compositions of the invention are well known and many such fluorescent agents are available commercially. Specific fluorescent agents which may be mentioned by way of example are:

(a) 4,4'di(2"-anilino-4"-morpholinotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(b) 4,4'-di(2"-anilino-4"-N-methylethanolaminotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(c) 4,4'-di(2"-anilino-4"-diethanolaminotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(d) 4,4-di(2"-anilino-4"-dimethylaminotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(e) 4,4'-di(2"-anilino-4"-diethylaminotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(f) 4,4'-di(2"-anilino-4"-monoethanolaminotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(g) 4,4'-di(2"-anilino-4"-(1-methyl-2-hydroxy)ethylaminotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(h) 4,4'-di(2"-methylamino-4"-p-chloroanilinotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(i) 4,4'-di(2"-dietholamine-4"-sulphanilinotriazin-6"-ylamino)-stilbene-2,2'-disulphonic acid and its salts,

(j) 4,4'-di(3-sulphostyryl)diphenyl and its salts,

(k) 4,4'-di(4-phenyl-1,2,3-triazol-2-yl)-stilbene-2,2'-disulphonic acid and its salts,

(l) 1-(p-sulphonamidophenyl)-3-(p-chlorophenyl)-Δ^2-pyrazoline.

The salt of the acid defined in (a) above, is referred to below as "fluorescer X".

Usually these fluorescent agents are supplied and used in detergent compositions in the form of their alkali metal salts, for example, the sodium salts. In addition to these fluorescent agents, the detergent composition of the invention may contain other types of fluorescent agents as desired. The total amount of the fluorescent agent or agents used in a detergent composition is generally from 0.02-2% by weight.

It is desirable to include one or more antideposition agents in the detergent compositions of the invention, to decrease a 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 2.5% by weight of the composition. The preferred antideposition agents are anionic polyelectrolytes, especially polymeric aliphatic carboxylates, or organic phosphonates.

It may be desirable to include in the compositions 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 compositions, 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 compositions of the invention are required to be alkaline, but not too strongly alkaline as this could result in fabric damage and also be hazardous for domestic usage. In practice the compositions should 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 pHs 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.

The detergent compositions of the invention should be in free-flowing particulate, eg powdered or granular form, and can be produced by any of the technique commonly employed in the manufacture of such washing compositons, but preferably by slurry making and spray drying processes to form a detergent base powder to which the ingredients of the bleach system, and optionally also the alkali metal tripolyphosphate are added. 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 as the lower moisture levels have been found to be beneficial for stability of the bleach systems employed.

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

EXAMPLE 1

The following base powders were prepared by spray drying a slurry containing the specified constituents:

Ingredient	Example 1	Comparative Example A
	(parts by weight)	
Anionic detergent active	6.5	6.5
Nonionic detergent active	3.0	3.0
Soap	5.0	5.0
STP	25.0	35.0
Zeolite (anhydrous)	13.0	-
Sodium silicate	2.0	6.0
Trimagnesium dequest*	-	0.12
Fluorescer X	0.2	0.2
Sodium sulphate, water and minor ingredients	21.39	20.27
	76.09	76.09

*Calculated as the equivalent amount of the acid form - Dequest 2041.

To these base powders were post-dosed the following ingredients:

Ingredient	Example 1	Comparative Example A
	(parts by weight)	
TAED	2.0	2.0
Sodium perborate	15.54	15.54
Dequest 2041	0.3	0.2
Sodium sulphate	6.07	6.17
	23.91	23.91

These powders were then tested using the following procedure. A Miele W484 automatic washing machine was used, set on its 60°C main wash only programme. The load used consisted of 4 kg of unsoiled cotton and 4 standard soiled bleach sensitive tea-stained test pieces. 100g of the test powder was introduced using the machine's dispenser. The machine's intake of water (hardness 15°FH) was 20 litres. Each powder was tested three times.

During the wash, samples of the wash liquor were taken when the wash liquor first reached 40°C. The content of peracetic acid and active oxygen was determined in each sample using conventional analytical techniques. At the end of each wash the bleaching performance on the standard test pieces was determined by measuring the reflectance at 460 nm on a Zeiss Elrepho photometer using a 420 nm UV interference filter (R 460*). The mean relectance of the samples before washing was 32.6 and the bleaching effect is quoted as a change in fabric reflectance, $\triangle$R460*.

The results obtained were as follows:

	Example 1	Example A
Peracetic acid yield (% theoretical)	72	71
Active oxygen yield (% theoretical)	85	84
$\triangle$ R460*	17.6	17.8

This Example demonstrates that the performance of the STP/zeolite product is surprising similar to the performance of the STP only product (Comparative Example A), despite the lower total-phosphorus level.

EXAMPLE 2

The experiments of Example 1 were repeated with powders made up according to the following formulations:

Ingredient	Example 2	Comparative Example B
	(parts by weight)	
Anionic detergent active	6.5	6.5
Nonionic detergent active	3.0	3.0
Soap	5.0	5.0
STP	18.0	-
Zeolite	21.0	40.0
Sodium silicate	6.0	6.0
Fluorescer X	0.2	0.2
Sodium sulphate, water and minor ingredients	14.8	13.8
	74.5	74.5
Post-dosed ingredients:		
TAED	2.0	2.0
Calcium dequest*	0.3	0.3
Sodium perborate	20.0	20.0
	22.3	22.3

* Calculated as the equivalent amount of the acid form - Dequest 2041.

The procedure of Example 1 was modified in that the experiment was carried out in a Tergotometer with a heat-up from 16°C to 60°C in 34 minutes. A product dosage of 5 g/l was used. The water hardness was 40° FH.

The results obtained were as follows:

	Example 2	Comparative Example B
Δ R460*	9.8	6.0

This example demonstrates that the bleaching performance of the STP/zeolite product is substantially better than the zeolite only product (Comparative Example B).

EXAMPLE 3

To the base powders given in Example 2 and in comparative Example B there were post-dosed the following ingredients:

Ingredient	Example 3	Comparative Example C
Base powder	Ex.2	Ex.B
TAED	3.0	3.0
Calcium dequest	-	-
Sodium perborate	6.0	6.0

Using the same procedure as in Example 2, modified only in that the water hardness was 35° FH, the results obtained were as follows:

	Example 3	Comparative Example C
Δ R 460*	4.7	2.2

EXAMPLE 4

To the base powders given in Example 2 and in Comparative Example B, there were post-dosed the following ingredients:

Ingredient	Example 4	Comparative Example D
Base powder	Ex.2	Ex.B
TAED	2.0	2.0
Calcium dequest	-	-
Sodium perborate	15.0	15.0

Using the same procedure as in Example 3, the following results were obtained:

	Example 4	Comparative Example D
Δ R460*	8.2	6.6

EXAMPLES 5 AND 6

Detergent powders were prepared according to the following approximate formulations and were found to give excellent results when compared with similar formulations in which sodium tripolyphosphate (STP) was the only builder material.

Example No:	5	6
Ingredients (% by weight)		
Anionic detergent active	6	6
Nonionic detergent active	4	4
STP	18	18
Zeolite	17	22
Sodium perborate	20	20
TAED	2.3	2.3
Suds-suppressant material	1.0	1.0
Sodium polyacrylate	0.9	-
Water, fluorescer and other convention ingredients	--- balance	---

The suds-suppressant material used was a 1:3 mixture of a C_{16} alkyl phosphoric acid ester and petroleum jelly with a drop melting point of 54°C.

EXAMPLE 7

The experiments of Example 1 were repeated with powders made up according to the following formulations (parts by weight):

Ingredient	Example	Comparative	Examples
	7	E	F
Anionic detergent active	6.5	6.5	6.5
Nonionic detergent active	3.0	3.0	3.0
Soap	5.0	5.0	5.0
STP (post-dosed)	18.0	32.0	-
Zeolite	21.0	-	30.0
Sodium silicate	6.0	6.0	6.0
Fluorescer X	0.2	0.2	0.2
TAED) post	2.0	2.0	2.0
Calcium Dequest*) dosed	0.3	0.3	0.3
Sodium perborate)	15.0	15.0	15.0
Sodium sulphate, water and minor ingredients	--------balance to 100--------		

* Calculated as the equivalent amount of the acid form - Dequest 2041.

The procedure of Example 1 was modified in that the experiment was carried out in a Tergotometer with a heat-up from 16°C to 55°C in 30 minutes. With a further 30 minutes at 55°C a product dosage of 5 g/l was used. Water hardnesses of 35°FH and 60°FH were used.

The results obtained were as follows:

ΔR460*	Example	Comparative	Example
	7	E	F
35°FH	16.5	18.2	18.8
60°FH	18.4	17.6	15.8

This Example demonstrates that the bleaching performance of the composition according to the invention (Example 7) is improved with increased water hardness, while the bleaching performance of the compositions based on STP only and zeolite only (Comparative Examples E and F) is reduced with increased water hardness.

EXAMPLE 8

The experiments of Example 1 were repeated with powders made up according to the following formulations (parts by weight):

Ingredient	Example 8	Comparative Example G
Anionic detergent active	6.5	6.5
Nonionic detergent active	3.0	3.0
Soap	5.0	5.0
STP (post-dosed)	18.0	18.0
Zeolite	21.0	21.0
Sodium silicate	6.0	6.0
Fluorescer X	0.2	0.2
TAED) post-	2.0	-
Sodium perborate) dosed	15.0	15.0
Sodium sulphate, water and minor ingredients	--------balance to 100--------	

The procedure of Example 1 was modified in that the experiment was carried out in a Tergotometer with a heat-up from 16°C to 55°C in 60 minutes. A product dosage of 5 g/l was used. Water hardnesses of 35°FH and 60°FH were used.

The results obtained were as follows:

Δ R460*	Example 8	Comparative Example G
35°F	10.8	7.7
60°F	16.0	7.0

This Example demonstrates that the bleaching performance of the composition according to the invention (Example 8) is improved with increased water hardness, while the bleaching performance of the composition containing perborate without TAED is reduced with reduced water hardness.

EXAMPLE 9

The following formulation represents a further exemplary detergent composition according to the invention.

Ingredient	% by weight
Anionic detergent active	11.0
Nonionic detergent active	5.0
Soap	5.0
STP (post-dosed)	18.0
Zeolite	17.0
Sodium perborate	12.0
TAED	2.0
Calcium dequest (calculated as the equivalent Dequest 2041)	0.3
Fluorescer X	0.2
Sodium silicate	6.0
Sodium polyacrylate	0.9
Water	10.0
Sodium sulphate and other conventional ingredients	balance

In the above examples, the anionic detergent active used was the sodium salt of alkyl (approx. C_{12}) benzene sulphonate and the nonionic used was a mixture of Dobanol 45-18 and Lutensol 12EO. The soap used was a mixture of hardened tallow soap and hardened rapeseed soap. The zeolite used was zeolite A (ex Degussa).

CLAIMS

1. A particulate alkaline detergent composition comprising at least one synthetic detergent active material, an alkali metal tripolyphosphate, a water-insoluble aluminosilicate detergency builder material, a peroxy bleach and an activator for said peroxy bleach, characterised in that it contains:

from about 5% to about 40% by weight of said synthetic detergent active material;

from about 12.5% to about 25% by weight of said alkali metal tripolyphosphate calculated on an anhydrous basis;

from about 7.0% to about 36% by weight of said water-insoluble aluminosilicate detergency builder material calculated on an anhydrous basis;

from about 5% to about 30% by weight of a peroxybleach; and

up to about 15% by weight of an activator for said bleach, the weight ratio of said peroxy bleach to said activator being between about 2:1 and about 15:1.

2. A composition according to Claim 1, characterised in that the sum of the percentage quantity of the alkali metal tripolyphosphate and half the percentage quantity of the aluminosilicate material lies between about 25 and about 37.

3. A composition according to Claim 1, characterised in that said at least one synthetic detergent active material is selected from anionic synthetic detergent active materials and mixtures thereof with a lesser amount of one or more non-anionic synthetic detergent active materials.

4. A composition according to Claim 1, characterised in that the at least one synthetic detergent active material includes an anionic detergent active material and a nonionic detergent active material in a relative weight ratio of at least 2:1.

5. A composition according to Claim 1, characterised in that it further contains a stabiliser for the bleach system.

6. A composition according to Claim 1, characterised in that it contains

from about 10% to about 25% by weight of a mixture of anionic detergent active material together with synthetic nonionic detergent active material, the weight ratio of said anionic material to said nonionic material being between about 3:1 and abour 10:1, the anionic material being a mixture of a synthetic anionic detergent active material and soap;

from about 15% to about 22% by weight sodium tripolyphosphate;

from about 12% to about 30% crystalline aluminosilicate detergency builder material;

from about 5.5% to about 27% by weight sodium perborate;

from about 0.5% to about 10% by weight tetraacetyl ethylene diamine, the weight ratio of the sodium perborate to the tetraacetyl ethylene diamine being between about 3.5:1 and about 10:1;

the balance of the composition, if any, being water, and optionally conventional detergent composition ingredients.

7. A particulate alkaline detergent composition substantially as hereinbefore described.

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EUROPEAN SEARCH REPORT

Application number

EP 82 30 0259.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	DE - A1 - 2 857 154 (PROCTER & GAMBLE EUROPEAN TECHNICAL CENTER) * claims 1 to 6; page 4, paragraph 3; page 11, paragraph 3; page 13, paragraph 3; page 25, paragraph 3; page 27, paragraph 3 to page 28, paragraph 1; page 34, examples * & GB - A - 2 040 981 --	1-7
X	DE - A1 - 2 902 236 (KAO SOAP CO.) * claims 1, 4, 12; pages 10, 11; page 12, paragraph 3, pages 19, 20; example 3 * --	1,3,7
X	DE - A1 - 2 655 578 (COLGATE-PALMOLIVE CO.) * claims 1, 2; page 15, paragraph 3 to page 16, paragraph 1 * --	1,3,6, 7
X	DE -A1 - 2 655 971 (COLGATE-PALMOLIVE CO.) * claims 1, 3, 7, 9; page 20 * & US - A - 4 064 062 --	1, 3-7
Y	DE - A1 - 2 655 482 (COLGATE-PALMOLIVE CO.) * claims 1, 3; page 1, paragraph 2; page 12; page 15, paragraph 1 * --	1,3,7

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CLASSIFICATION OF THE APPLICATION (Int. Cl. ^{3})

C 11 D 3/12
C 11 D 3/39

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	02-03-1982	SCHULTZE

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EUROPEAN SEARCH REPORT

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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 - 2 656 285 (COLGATE-PALMOLIVE CO.) * claims 1, 4, 6, 8; page 23 * & FR - A1 - 2 335 598 & US - A - 4 055 505 --	1,3,5, 7	
A	FR - A1 - 2 398 798 (BASF AG) * claims 1, 3; page 6 * & GB - A - 2 003 205 ----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.³)