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WASHING AND CLEANSING COMPOSITIONS
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6 Claims

ABSTRACT OF THE DISCLOSURE

Builder salt-containing washing and cleansing compositions comprising (a) one part by weight of a capillary-active compound selected from the group consisting of anionic surface-active compounds, non-ionic surface-active compounds and amphoteric surface-active compounds and (b) 0.5 to 20 parts by weight of a mixture of builder salts consisting of (1) from 25% to 75% by weight of said mixture of pentasodium triphosphate, (2) from 10% to 50% by weight of said mixture of sodium citrate, and (3) from 10% to 60% by weight of said mixture of sodium carbonate.

THE PRIOR ART

As is known, washing and cleansing agents often contain larger amounts of condensed metal phosphates, particularly pentasodium triphosphate, also known as sodium tripolyphosphate. The phosphates are utilized in the washing agent composition to complex and bind the hardness constituents of tap water and to increase the cleansing activity of the surface-active detergents. For various reasons, however, an increase of the phosphate content of the agents above a certain percentage should not be attempted or a decrease in respect to the share customary up to now should not be attempted. Therefore, the objective existed partly to replace the polyphosphates, contained in the washing and cleansing agents, by other substances free of phosphates and to improve at the same time the cleansing power and the biological degradability of the mixtures.

OBJECTS OF THE INVENTION

An object of the invention is the obtaining of a washing and cleansing composition containing builder salts which has a lower phosphate content and an improved cleansing activity and capability to complex and bind the hardness constituents of tap water.

Another object of the invention is the obtaining of builder salt-containing washing and cleansing compositions comprising (a) one part by weight of a capillary-active compound selected from the group consisting of anionic surface-active compounds, non-ionic surface-active compounds and amphoteric surface-active compounds and (b) 0.5 to 20 parts by weight of a mixture of builder salts consisting of (1) from 25% to 75% by weight of said mixture of pentasodium triphosphate, (2) from 10% to 50% by weight of said mixture of sodium citrate, and (3) from 10% to 60% by weight of said mixture of sodium carbonate.

These and other objects of the invention will become more apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

It has now been found that the drawbacks of the prior art have been overcome and the above objects achieved by builder salt-containing washing and cleansing compositions comprising (a) one part by weight of a capillary-active compound selected from the group consisting of anionic surface-active compounds, non-ionic surface-active compounds and amphoteric surface-active compounds and (b) 0.5 to 20 parts by weight of a mixture of builder

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salts consisting of (1) from 25% to 75%, preferably from 35% to 65%, by weight of said mixture of pentasodium triphosphate, (2) from 10% to 50%, preferably from 15% to 40%, by weight of said mixture of sodium citrate, and (3) from 10% to 60%, preferably from 15% to 50%, by weight of said mixture of sodium carbonate.

Of particular interest are washing agents with a low foaming power, suitable for use in drum-washing machines. So far as the capillary-active surface-active substances utilized in the washing agents have a tendency for strong foaming, the agents should contain 0.01 to 1 part by weight of at least one foam inhibitor. Suitable foam inhibitors are saturated fatty acids with 18 to 24 carbon atoms or their alkali metal salts, which particularly contain higher amount of arachinic acid, behenic acid, and lignoceric acid and can be obtained, for instance, from hardened peanut, rape and fish oil. Further suitable foam inhibitors are the triazine derivatives, such as N,N',N"-trialkylmelamine or 2,4-diaminoalkyl-6-chloro-1,3,5-triazine, in which the alkyls have 6 to 24 carbon atoms, also propoxylated and/or butoxylated melamines with 6 to 100 polyglycolether groups, for example, melamine reacted with 10 to 100 mols of propylene oxide or one reacted with 6 to 30 mols of butylene oxide, or one reacted first with 3 to 30 mols of propylene oxide and subsequently with 3 to 30 mols of butylene oxide. Also mixtures of the above-named foam inhibitors may be used advantageously. Preferably, the amount of the foam inhibitors added is calculated to be from 1% to 30% by weight based on the amount of the foaming surface-active substances in the washing agent composition.

Optionally, paraffin hydrocarbons, halogenated paraffins, higher molecular weight fatty acid esters or triglycerides or dicarboxylic acid esters of higher molecular weight fatty alcohols may also be used as foam reducing agents or in a mixture with the above-named foam inhibitors. The foam reducing effect of these substances is, however, less than that of the above-named foam inhibitors, particularly if the washing agents are free of soap. Appropriately they are, therefore, only used in agents containing soap.

The washing and cleansing agents can contain conventional anionic basic detergent substances of the sulfonate or sulfate type. Primarily alkylbenzene sulfonates, for example, dodecylbenzene sulfonate are suitable, also olefin sulfonates, such as, for example, are obtained by sulfonation of primary and secondary aliphatic monoolefins with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis, as well as alkylsulfonates obtainable from n-alkanes by sulfochlorination or sulfoxidation and subsequent hydrolysis or neutralization, or by addition of bisulfite to olefins. Also suitable are α -sulfofatty acid esters, primary and secondary alkylsulfates and the sulfates of ethoxylated or propoxylated higher alcohols. Other compounds of this class which can be optionally present in the washing composition are the higher molecular weight sulfated partial ethers and partial esters of polyhydric alcohols, such as the alkali metal salts of the monoalkyl ethers or mono fatty acid esters of the glycerine monosulfuric acid esters, or 1,2-dihydroxypropanesulfonic acid. Also sulfates of ethoxylated or propoxylated fatty amides and alkylphenols as well as fatty acid taurides and fatty acid isothionates are suitable.

Other appropriate anionic basic detergent ingredients are alkali metal soaps of natural or synthetic fatty acids, such as sodium soaps of coconut, palm kernel, or tallow fatty acids. As amphoteric detergent components, alkyl betaines and particularly alkyl sulfobetaines are suitable, for example, 3-(N,N-dimethyl-N-alkylammonium)-propane-1-sulfonate and 3-(N,N-dimethyl-N-alkylammonium)-2-hydroxypropane-1-sulfonate.

The anionic basic detergent ingredients can be present

in the form of their alkali metal salts such as the sodium and potassium, and ammonium salt, as well as salts of organic bases, such as mono-, di- and triethanolamine. Inasmuch as the named anionic and amphoteric compounds have an aliphatic hydrocarbon radical, the latter should preferably be straight-chained and should have from 8 to 22 carbon atoms. In the compounds with araliphatic hydrocarbon radicals, such as alkylphenyl radicals, the preferred straight alkyl chains contain an average of from 6 to 16 carbon atoms.

As non-ionic surface-active basic detergent ingredients, primarily suitable are the polyglycoether derivatives of alcohols, fatty acids and alkylphenols which contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the hydrocarbon radical. Particularly suitable are polyoxyethyleneglycoether derivatives in which the number of oxyethylene groups is 5 to 15 and whose hydrocarbon radicals are derived from straight-chain primary alcohols with 12 to 18 carbon atoms, or from alkylphenols with a straight-chain alkyl chain of 6 to 14 carbon atoms. By the addition of 3 to 15 mols of propylene oxide to the last named polyethyleneglycoethers, or by converting them into acetals, detergents are obtained which are distinguished by a special low foaming power.

Other suitable non-ionic basic detergent ingredients are the water-soluble polyethylene oxide adducts, containing 20 to 250 ethyleneglycoether groups and 10 to 100 propyleneglycoether groups adducted to polypropylene glycol, ethylenediamine-polypropyleneglycol and alkylene-polypropyleneglycol with 1 to 10 carbon atoms in the alkylene chain. The compounds utilized usually contain 1 to 5 oxyethylene units per oxypropylene unit. Also suitable as non-ionic compounds are those of the amine oxide and sulfoxide types, which, if necessary can be ethoxylated.

By a suitable combination of different surface-active basic detergent substances with one another, increases in activity may be obtained in many cases, for example, an improved washing power or a reduced foaming capacity. Such improvements are possible, for example, by a combination of anionic compounds with non-ionic and/or amphoteric compounds, by a combination of different non-ionic compounds, or by mixtures of basic detergent substances of the same type which differ in regard to the number of carbon atoms or the number and position of double bonds or branching of chains.

Depending on their use, the cleaning compositions of the invention may also contain oxygen-yielding or active chlorine-containing bleaching agents such as hydrogen peroxide, alkali metal perborates, particularly sodium perborate, alkali metal percarbonates, alkali metal perphosphates, urea perhydrate, alkali metal persulfate, alkali metal hypochlorites, chlorinated trisodium phosphate and chlorinated cyanuric acid and its alkali metal salts. The per-compounds can be present in admixture with bleaching agent activators.

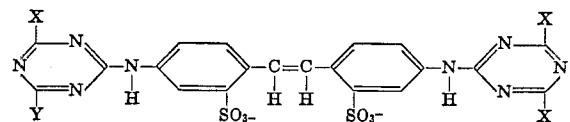
In addition to the surface-active compounds, builder salts, foam inhibitors and bleaching agents, the washing and cleaning agents of the invention may contain other customary washing agent ingredients. These include sodium sulfate, silicates, such as magnesium silicate, utilized as a perborate stabilizer, and water glass, utilized as a corrosion inhibitor, with a $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of from 1:3 to 1:3.5. In addition, the agents may contain tetrasodium pyrophosphate which might be formed during the compounding, particularly with the hot spray-drying of the liquid washing agent concentrates, by a partial hydrolysis of the sodium tripolyphosphate.

Further suitable mixture ingredients are anti-greying or soil anti-redeposition compounds, such as sodium cellulose glycolate, as well as the water-soluble alkali metal salts of synthetic polymers which contain free carboxylic groups. To them belong the polyesters of the polyamides of tri- and tetracarboxylic acids and dihydric alcohols or diamines, also polymeric acrylic, methacrylic, maleic,

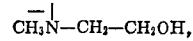
fumaric, itaconic, citraconic and aconitic acids, as well as the mixed polymerizates of the above-named unsaturated carboxylic acids or their mixed polymerizates with olefins.

For a further improvement of the dirt loosening properties of the washing and cleaning compositions of the invention, they may also contain enzymes from the class of the proteases, lipases and amylases, which may be obtained from animal and vegetable origin, for example, from digestive ferments or yeasts, such as pepsin, pancreatin, trypsin, papain, catalase and diastase. Preferably, enzymic active substances are obtained from strains of bacteria or fungi, such as *Bacillus subtilis* and *Streptomyces griseus*, which substances are relatively stable towards alkalis, percompounds and anionic detergent substances and are not appreciably inactivated even at temperatures between 45° C. and 70° C.

Further suitable components of the mixtures are optical brighteners of the bis-(triazinyl)-4,4'-diaminostilbene-disulfonic acid type according to the following formula

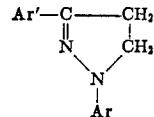


25 in which X and Y represent the following: $-\text{NH}_2$, $-\text{NH}-\text{CH}_3$, $-\text{NH}-\text{CH}_2-\text{CH}_2\text{OH}$,



30 $-\text{N}(\text{CH}_2-\text{CH}_2\text{OH})_2$, morpholino, dimethylmorpholino, $-\text{NH}-\text{C}_6\text{H}_5$, $-\text{NH}-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$, $-\text{OCH}_3$, $-\text{Cl}$, where X and Y are the same or different. Compounds in which X represents an anilino and Y a diethanolamino or morpholino group are specially suitable.

35 In addition, optical brighteners of the diarylpyrazoline type according to the following formula may be present:



In the formula, Ar and Ar' represent aryl residues, such as phenyl, diphenyl or naphthyl, which may carry further substituents such as hydroxy, alkoxy, hydroxylalkyl, amino, alkylamino, acylamino, carboxyl, sulfonic acid and sulfonamide groups or halogen atoms. 1,3-diarylpyrazolines are preferably used in which Ar is p-sulfonamido-phenyl and Ar' is p-chlorophenyl. In addition, whiteners suitable for the brightening of other types of fibers may be present, for example, such as of the type of naphtho-triazolestilbene sulfonates, ethylene-bis-benzimidazoles, ethylene-bis-benzoxazoles, thiophene-bis-benzoxazoles, dialkylaminocoumarins, and cyanoanthracenes. These brighteners or their mixtures can be present in the washing composition in amounts from 0.01% to 1.5% by weight, preferably from 0.1% to 1% by weight.

For stabilizing of the optical brighteners, the agents can also contain complexing agents. To these belong the alkali metal salts of ethylenediaminetetraacetic acid, which are preferably used. In addition, the alkali metal salts of diethylenetriaminepentaacetic acid as well as the higher homologs of the named aminopolycarboxylic acids can be present. Suitable homologs can, for instance, be prepared by polymerization of an ester, amide or nitrile of N-acetic acid-aziridine and subsequent saponification to carboxylic acid salts, or by reacting a polyamine with a molecular weight of from 500 to 100,000 with alkali metal chloroacetates or bromoacetates in an alkaline medium. Other suitable complexing agents are the alkali metal salts of aminopolyposphonic acids, particularly aminotri(methylene-phosphonic acid), ethylenediamine-tetra-(methylene-phosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, methylene-diphosphonic acid, ethylene-diphosphonic acid as well as the higher homologs of the

named polyphosphonic acids. Also mixtures of the above-named complexing agents are usable.

Furthermore, bactericidal substances, particularly halogenated diphenylethers, halogenated diphenylurea derivatives and halogenated salicylic acid anilides can be present. For the improvement of the hand, non-quaternary, higher molecular weight, ammonium compounds may be added, such as the tallow fatty acid amide of the aminoethylethanolamines.

The washing and cleaning agents may be present in liquid, pasty or, preferably, solid form, for example, pulverulent, granulated or lump form, and particularly spray dried. For better solubility, liquid preparations may contain solvents miscible with water, especially ethanol and isopropanol, as well as solution aids such as the alkali metal salts of benzene-, toluene-, xylene- or ethylbenzene-sulfonic acid.

In the preparation of the washing agents of the invention, the sodium citrate, as such, is mixed directly with the other washing agent ingredients or with the aqueous pasty washing agent mixture, or the free citric acid is added to these mixtures, provided that they contain an excess of alkaline-reacting compounds required for neutralization, for instance, sodium hydroxide or sodium carbonate. In this case the salt is formed during the preparation or the use of the agent.

If the agents contain foam inhibitors from the class of substituted triazines or melamines, the latter are advantageously admixed to the washing agent ingredients present as powder or granulate, or to a part of them, granulated upon them or in melted form or, after dissolving in a volatile solvent, sprayed upon them.

The quantitative composition of the agents of the invention corresponds preferably to the following recipe:

1 part by weight of a surface-active compound which consists by weight of up to 100%, preferably 5% to 70%, of compounds of the sulfonate and/or sulfate type, up to 100%, preferably 5% to 40%, of non-ionic compounds of the polyglycoether type, and up to 100%, preferably 10% to 50%, of soap,

0.5 to 20, preferably 1 to 10, parts by weight of the builder salt mixture consisting of pentasodium tripophosphate, sodium citrate, and sodium carbonate,

0.01 to 1 part, preferably an amount which is 1% to 30%, by weight of the surface-active detergents, of foam inhibitors, preferably from the class of saturated fatty acids with 18 to 24 carbon atoms and their alkali metal soaps, as well as of the substituted triazines, obtainable by the reaction of 1 mol of cyanuric chloride with 2 to 3 mols of a primary monoamine, or by propoxylation and/or butoxylation of melamine,

0 to 5, preferably 0.5 to 3, parts by weight of sodium perborate with or without crystalline water,

0 to 3, preferably 0.1 to 2, parts by weight of other washing agent ingredients which have preferably the following composition:

0.1% to 80% of neutral salts, particularly sodium sulfate,

0 to 40% of tetrasodium pyrophosphate,

0 to 10% of sodium ethylenediaminetetraacetate,

0 to 40% of magnesium silicate,

0.1% to 20% of greying inhibitors, particularly sodium carboxymethylcellulose,

0 to 20% of enzymes, and

0 to 10% of at least one optical brightener.

The agents according to the invention possess a high cleansing power and an improved dirt-carrying power. The effects are greater than if each of the three components of the salt mixture, named under (b), were present alone. On the basis of the reduced phosphate content, the washing agents are distinguished by a good biological degradability and they do not promote the undesirable growth of algae and plants in rivers and lakes burdened by sewage. In comparison with mixtures which contain

as builder salts, exclusively or predominately, sodium tripophosphate, they cause in repeated application, a reduction in fabric incrustation and in damage of the textile fibers.

The following examples are illustrative of the practice of the invention without, however, being deemed limitative in any respect.

EXAMPLES 1 TO 16

The washing agents used had the compositions shown in Table I (data in percent by weight).

TABLE I

Ingredients	A	B	C	D
n-Dodecylbenzene sulfonate (Na-salt).....	14.0			9.5
α -Olefin sulfonate (Na-salt).....		14.0		
n-Alkane sulfonate (Na-salt).....			14.0	
15 Ethoxylated oleyl alcohol (9 EtO).....	2.5	2.5	2.5	2.5
Fatty acid from hydrogenated rape oil.....	1.0	1.0	1.0	1.0
Coconut-tallow soap (Na-salt).....	2.5	3.5	3.5	4.5
Ethylenediaminetetraacetate (Na-salt).....				0.2
Tetrasodium pyrophosphate.....	9.0	8.0	8.0	5.0
Sodium water glass ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.3$).....	4.0	4.0	4.0	4.0
20 Sodium perboratetetrahydrate.....	16.0	20.0	20.0	20.0
Sodium sulfate.....	8.0	3.0	3.0	3.0
Carboxymethylcellulose (Na-salt).....	1.7	1.5	1.5	1.7
Optical brightener.....				0.5
Water.....	7.3	7.5	7.5	7.1
Builder salts.....	34.0	35.0	35.0	40.0

The olefin sulfonate was derived from straight-chain $\text{C}_{15}-\text{C}_{18}$ olefins (average chain length $\text{C}_{16.5}$). The alkane sulfonate was a product prepared from n-paraffins of a chain length of $\text{C}_{14}-\text{C}_{17}$ by sulfoxidation and contained secondary sulfonate groups. The abbreviation EtO stands for ethylene oxide groups. No optical brightener was added to the agents A, B and C in order not to partially mask the results of the determination of the degree of whiteness by fluorescence phenomena.

The composition of the mixture designated by "builder salts" can be found in Table II. The compounds were used as sodium salts.

For the determination of the washing power, textile samples of cotton that had been homogeneously soiled with a mixture of dust and skin fat were washed in a laboratory washing machine (Launder-Ometer). The washing agents concentration was 4 gm./liter. The weight ratio of washing liquor to textile was 12:1. The temperature was 90° C., and the washing time 15 minutes. The tap water used had a hardness of 16° dH (corresponding to 160 mgm. CaO/l). The whiteness degree of the three-times rinsed and then dried fabric was determined by photometer. The results are summarized in Table II. Each test series was preceded by comparative tests in which the builder consisted of only one component. The results demonstrate the superiority of the mixture of builder salts of the invention.

TABLE II

Example	Wash-ing agent	Composition of the builder salts			
		Triphos-phate, percent	Citrate, percent	Carbonate, percent	Degree of whiteness
55	A	100			76
	A		100		76
	A			100	75
1	A	45	25	30	78
2	A	60	25	15	78
3	A	45	35	20	78
4	A	60	15	25	78
5	A	30	25	45	77
	B	100			75
	B		100		75
	B			100	73
6	B	45	25	30	78
7	B	60	25	15	77
8	B	45	35	20	77
9	B	60	15	25	77
10	B	30	25	45	76
	C	100			75
	C		100		75
	C			100	74
11	C	45	25	30	78
12	C	60	25	15	77
13	C	45	35	20	77
14	C	60	15	25	77
	D	100			78
	D		100		79
15	D	45	25	30	78
16	D	60	25	15	80
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The preceding specific embodiments are illustrative of the practice of the invention. It is to be understood, however, that other expedients known to those skilled in the art, or disclosed herein, may be employed without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. Builder salt-containing washing and cleansing compositions consisting essentially of (a) one part by weight of a capillary-active compound selected from the group consisting of anionic surface-active compounds, nonionic surface-active compounds and amphoteric surface-active compounds and (b) 0.5 to 20 parts by weight of a mixture of builder salts consisting of (1) from 30% to 60% by weight of said mixture of sodium tripolyphosphate, (2) from 15% to 35% by weight of said mixture of sodium citrate, and (3) from 15% to 45% by weight of said mixture of sodium carbonate.

2. The builder salt-containing washing and cleansing compositions of claim 1 having a further content of from 0.01 to 1 part by weight of at least one foam inhibitor selected from the group consisting of saturated fatty acids having 18 to 24 carbon atoms and their alkali metal soaps, N,N',N'' - trialkylmelamines and 2,6 - diaminoalkyl - 6-chloro-triazines wherein the alkyl radicals have 6 to 24 carbon atoms, and alkoxylated melamines having from 6 to 100 polyglycoether groups selected from the group consisting of propyloxyLATED melamines, butyloxyLATED melamines and propyloxyLATED, butyloxyLATED melamines.

3. The builder salt-containing washing and cleansing compositions of claim 1 wherein capillary-active compounds are selected from the group consisting of sulfate and sulfonate anionic surface-active compounds, polyglycoether non-ionic surface-active compounds and soaps.

4. The builder salt-containing washing and cleansing compositions of claim 3 wherein said capillary-active compounds consist of a mixture of from 25% to 70% by weight of sulfonate and sulfate anionic surface-active compounds, from 5% to 40% by weight of polyglycoether non-ionic surface-active compounds and from 10% to 50% by weight of soap.

5. The builder salt-containing washing and cleansing compositions of claim 1 having a further content of from 0.1 to 5 parts by weight of sodium perborate.

6. Builder salt-containing washing and cleansing compositions consisting essentially of (a) one part by weight

of a mixture of capillary-active compounds consisting of from 25% to 70% by weight of sulfonate and sulfate anionic surface-active compounds, from 5% to 40% by weight of polyglycoether non-ionic surface-active compounds and from 10% to 50% by weight of soap, (b) from 1 to 10 parts by weight of a mixture of builder salts consisting of from 30% to 60% by weight of said mixture of sodium tripolyphosphate, from 15% to 35% by weight of said mixture of sodium citrate and from 15% to 45% by weight of said mixture of sodium carbonate, (c) from 1% to 30%, based on the weight of said mixture of capillary-active compounds of a foam inhibitor selected from the group consisting of saturated fatty acids having 18 to 24 carbon atoms and their alkali metal soaps, N,N',N'' - trialkylmelamines and 2,6-diaminoalkyl-6-chloro-triazines wherein the alkyl radicals have 6 to 24 carbon atoms, and alkoxylated melamines having from 6 to 100 polyglycoether groups selected from the group consisting of propyloxyLATED melamines, butyloxyLATED melamines and propyloxyLATED, butyloxyLATED melamines, (d) from 0.5 to 3 parts by weight of sodium perborate and (e) from 0.1 to 2 parts by weight of other washing agent ingredients consisting of 0.1% to 80% by weight of neutral salts, 0 to 40% by weight of tetrasodium pyrophosphate, 0 to 10% by weight of sodium ethylene diaminetetraacetate, 0 to 40% by weight of magnesium silicate, 0.1% to 20% by weight of soil anti-redeposition agents, 0 to 20% by weight of enzymes and 0 to 10% by weight of optical brighteners.

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References Cited

UNITED STATES PATENTS

2,817,606	12/1957	Barrett	-----	134-22
3,368,978	2/1968	Irani	-----	252-137
3,954,348	9/1960	Schwoeppe	-----	252-109
3,422,020	1/1969	Schmadel	-----	252-99
2,264,103	11/1941	Tucker	-----	210-23
3,235,505	2/1966	Tuvell	-----	252-135

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