Abstract:

Title: CLEANING COMPOSITION CONTAINING SUBSTITUTED STARCH

A cleaning composition comprising from 0.05% to 30% by weight of surfactant and from 0.01% to 10% by weight of substituted starch, wherein the substituted starch has: - a total degree of substitution in the range of from 0.001 to 0.6, - a degree of substitution of anionic substituent in the range of from 0.001 to 0.04 and/or a degree of substitution of nonionic substituent in the range of from 0.01 to 0.5, - a degree of substitution of cationic substituent in the range of from 0 to 0.004, - an average per weight molecular weight in the range of from 10 000 to 100 000 000 Daltons.
CLEANING COMPOSITION CONTAINING SUBSTITUTED STARCH

FIELD OF THE INVENTION

The present invention relates to a cleaning composition comprising starch substituted with anionic and/or nonionic substituent. More particularly, the substituted starch in the present invention provide suds boosting benefit, such as suds volume and suds duration enhancement, to cleaning compositions such as fabric care products, dish care products, oral care product, or applications where cleaning of surfaces is needed.

BACKGROUND OF THE INVENTION

Cleaning compositions must satisfy several criteria in order to be effective and fulfill the need of the consumer. In particular, the presence of suds in a cleaning operation has long been used as a signal that the detergent continues to be effective. However, depending upon the circumstances, the presence of suds or the lack thereof, may have little or no bearing upon the efficacy of the cleaning process. Therefore, the consumer who relies upon a somewhat erroneous signal may tend to use an excess of cleaning product in the lack or absence of suds.

Accordingly, there remains a need for adjusting the sudsing properties of a cleaning composition with flexibility, in particular to adjust the sudsing properties relatively independently from the cleaning properties. This is especially needed for cleaning composition comprising a low level of surfactant or of builder.

The inventors have discovered that some or all of the above mentioned needs could be at least partially fulfilled in the cleaning composition of the invention by using a specific substituted starch.

Unless otherwise specified, all percentage and ratio are in weight

SUMMARY OF THE INVENTION

The present disclosure relates to a cleaning composition comprising from 0.05% to 30% by weight of surfactant and from 0.01% to 10% by weight of substituted starch polymer, wherein the substituted starch has:
- a total degree of substitution in the range of from 0.001 and 0.6,
- a degree of substitution of anionic substituent in the range of from 0.001 to 0.04 and/or a degree of substation of nonionic substituent in the range of from 0.01 to 0.5,
a degree of substitution of cationic substituent in the range of from 0 to 0.004,
an average per weight molecular weight in the range of from 10 000 to 100 000 000 Daltons.

According to an embodiment of the invention, the invention concerns the use of a substituted starch, wherein the substituted starch has:
- a total degree of substitution in the range of from 0.001 and 0.6,
- a degree of substitution of anionic substituent in the range of from 0.001 and 0.04 and/or a degree of substation of nonionic substituent in the range of from 0.01 and 0.5,
- a degree of substitution of cationic substituent in the range of from 0 to 0.004,
an average per weight molecular weight in the range of from 10 000 to 100 000 000 Daltons,
to increase the quantity of suds that can be generated by a cleaning composition.

DETAILED DESCRIPTION OF THE INVENTION

Starch

The cleaning composition of the invention comprises from 0.01% to 10% by weight of one or more substituted starch. Preferably, the cleaning composition of the invention comprises from 0.1% to 7% by weight of substituted starch, in particular from 0.1% to 5%, typically from 0.3% to 3% by weight of substituted starch polymer.

The starch polymer comprises sugar monomers. The sugar monomers can be substituted or not substituted. When the sugar monomer is substituted, one or more of its hydroxy function may be substituted.

The substituted starch of the invention has a total degree of substitution (DSt) in the range of from 0.001 to 0.6. Typically, the substituted starch has a DSt of in the range of from 0.003 to 0.3, in particular in the range of from 0.01 to 0.2.

DSt corresponds to the ratio between the sugar monomers which are substituted to the total number of sugar monomers of the starch polymer. If all the sugar monomers are substituted at least once, the value of DSt is 1.

The substituted starch of the invention has a DSt in the range of from 0.001 and 0.6, typically between 0.01 and 0.5.

For the purpose of this disclosure, degree of substitution of a specific substituent refers to the ratio of sugar monomers which are substituted at least once with said specific substituent to the total number of sugar monomers of the starch polymer.
DSa corresponds to the ratio between the sugar monomers of the starch polymer which are substituted with at least one anionic substituent and the total number of sugar monomers of the starch polymer. If all the sugar monomers are substituted with at least one anionic substituent, the value of DSa is 1.

DSn corresponds to the ratio between the sugar monomers of the starch polymer which are substituted with at least one nonionic substituent and the total number of sugar monomers of the starch polymer. If all the sugar monomers are substituted with at least one nonionic substituent, the value of DSn is 1.

DSc corresponds to the ratio between the sugar monomers of the starch polymer which are substituted with at least one cationic substituent and the total number of sugar monomers of the starch polymer. If all the sugar monomers are substituted with at least one cationic substituent, the value of DSc is 1.

For the purpose of this disclosure, a substituent is considered anionic, cationic or nonionic, depending of its net charge value at a pH of 10.

The substituted starch of the invention has a degree of substitution of anionic substituent (DSa) in the range of from 0.001 to 0.04 and/or a degree of substitution of nonionic substituent (DSn) in the range of from 0.01 to 0.5. The substituted starch of the invention may have a degree of substitution of anionic substituent in the range of from 0.001 to 0.04, preferably in the range of from 0.003 to 0.02, in particular in the range of from 0.01 to 0.01. The substituted starch of the invention may have a degree of substitution of nonionic substituent in the range of from 0.01 and 0.5, preferably in the range of from 0.03 to 0.3, in particular in the range of from 0.08 to 0.15.

The substituted starch of the invention has a degree of substitution of cationic substituent DSc in the range of from 0 to 0.004. Preferably, the substituted starch has a DSc in the range of from 0 to 0.02, typically in the range of from 0 to 0.001 or from 0 to 0.0005 or from 0 to 0.0002 or even from 0 to 0.0001 or from 0 to 0.00002. Preferably, the DSc is below the DSa. As such, the substituted starch has preferably an overall net negative charge. Typically, the ratio DSc to DSa, per number of substituent, is below 1, typically below 0.9 or 0.75 or 0.5, or even below 0.3 or 0.1 or 0.05 or 0.01 or 0.001.

The inventors have found that substituted starch comprising a low DSc, in particular having a DSc below the DSa, were particularly suitable for providing the sudsing benefit of the invention.

The substituted starch of the invention has an average per weight molecular weight in the range of from 10 000 to 100 000 000 Daltons. Preferably the substituted starch has an average per weight molecular weight of from 20 000 to 50 000 000 Daltons.

Preferably, when the substituted starch has a DSa above 0.001, for example above 0.005 or 0.01, the substituted starch has an average per weight molecular weight in the range
of from 20 000 to 500 000 Daltons, preferably in the range of from 40 000 to 200 000 or from 70 000 to 150 000.

According to an exemplary embodiment of the invention, the substituted starch has a DSa above 0.01, and a DSc above 0.01. Preferably, when the substituted starch has a DSa above 0.01, and a DSc above 0.01, the substituted starch has an average per weight molecular weight in the range of from 100 000 to 100 000 000 Daltons, preferably in the range of from 200 000 to 50 000 000 or from 500 000 to 10 000 000 or even from 1 000 000 to 5 000 000.

The substituted starch may have a degree of substitution of nonionic hydroxyalkyl substituent in the range of from 0.01 and 0.5. In particular, the substituted starch has a degree of substitution of nonionic hydroxyalkyl substituent in the range of from 0.03 to 0.3, or from 0.08 to 0.15.

The substituted starch may have a degree of substitution of anionic substituent comprising a sulphate or sulphonate group in the range of from 0.001 and 0.4, preferably in the range of from 0.003 to 0.1, in particular in the range of from 0.005 to 0.2.

The inventors have found that starches substituted with anionic substituent comprising a sulphate or sulphonate group or with nonionic hydroxyalkyl substituent were particularly suitable to provide the sudsing benefit of the invention.

Starch comprises amylose (see formula I below) and amylopectin (see formula II below). Starch is described in Kirk-Othmer’s Encyclopedia of Chemical Technology 4th Edition, Vol. 22, at pp. 699-719.

The substituted starch may comprise substituted polymers selected from polymers of general formula:

\[
\begin{align*}
\left( \begin{array}{c}
\text{CH}_2\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\text{OR} \\
\end{array} \right)_{n}
\end{align*}
\]
and mixtures thereof, wherein each R is H or a substituent selected from the group of anionic substituent, nonionic substituent, and cationic substituent, wherein at least 70% by number of the R are H, the degree of substitution of anionic substituent is in the range of from 0 to 0.04, the degree of substitution of nonionic substituent is in the range of from 0 to 0.5, the degree of substitution of cationic substituent is in the range of from 0 to 0.004, wherein either the degree of substitution of anionic substituent is of at least 0.002 or the degree of substitution of non-ionic is of at least 0.02, wherein n is such that said suds boosting substituted polymer(s) has an average per weight molecular weight ranging from 20 000 Daltons to 100 000 000 Daltons.

Suitable anionic, nonionic, or cationic substituents may be selected from the group consisting of branched, linear or cyclic, substituted or not substituted, saturated or unsaturated alkyl, amine (primary, secondary, tertiary), ammonium salt, amide, urethane, alcohol, carboxylic acid, tosylate, sulfonate, sulfate, nitrate, phosphate, silicone, and mixtures thereof.

The anionic, nonionic, and cationic substituents may be selected from the group consisting of: R_1, N(R_2)(R_s), silicone moiety, S(V, P(V, with R_2 and R_3 being independently of each other an hydrogen atom or a C_{6} alkyl and R_i being a linear or branched, typically linear, saturated or unsaturated, typically saturated, substituted or unsubstituted, typically substituted, cyclic or acyclic, typically acyclic, aliphatic or aromatic, typically aliphatic, C_{300}, typically C_{1}-C_{30}, C_{1}-C_{2}, or C_{1}-C_{6} hydrocarbon radical which hydrocarbon backbone may be interrupted by a heteroatom chosen form O, S, N and P. R_i may be substituted by one
or more radical selected from amino (primary, secondary, or tertiary), amido, -OH, -CO-OR₄,
-SO₃⁻, R₄⁻, -CN, and -CO-R₄, where R₄ represents a hydrogen atom or an alkali metal,
preferably a sodium or potassium, ion.

The anionic substituent may be one following anionic groups, in its acid or salt form, preferably sodium (given here) or potassium salt form:

- T-CO₂Na
- T-SO₃Na
- PO₄Na
- SO₃Na

Wherein T is a Cl-6 alkyl, more preferably Cl-4 alkyl.

The cationic substituent may be the following cationic group:

\[
\begin{array}{c}
\text{X}^O \\
\text{I} \\
\text{C}
\end{array}
\]

Wherein T is a Cl₆ alkyl, or CH₂CH(OH)CH₂, each A, B, and C is Cl₆ alkyl or
hydroxy-Cl₆ alkyl, X is a counterion such as halide or tosylate.

The nonionic substituent may be one following non-ionic groups:

- A
- T-OH
- T-CN
- C(=0)A
- C(=0)NH₂
- C(=0)NHA
- C(=0)N(A)B
- C(=0)OA
- (CH₂CH₂CH₂O)ₙZ
- (CH₂CH₂O)ₙZ
- (CH₂CH(CH₃)O)ₙZ
- (CH₂O)ₙZ

Wherein: A and B are Cl₃₀ alkyl; T is Cl₆ alkyl; n = 1 to 100; Z is H or Cl₆ alkyl.
Preferably the anionic substituent comprises a sulphate or sulphonate group. Preferably the nonionic substituent is a nonionic hydroxyalkyl wherein the alkyl is a C1-C6 alkyl, in particular a C1-C4 or C1-C3 or C1-C2 alkyl.

Preferably, the ratio of the degree of substitution of anionic substituent comprising a sulphate or sulphonate group to the total degree of substitution of anionic substituent is in the range of from 1:5 to 1:1, preferably above 1:3 or 1:2 or even 1:1.5 or 1:1.2 or 1:1.1.

Preferably, the ratio of the degree of substitution of nonionic hydroxyalkyl substituent wherein the alkyl is a C1-C6 alkyl, to the total degree of substitution of nonionic substituent is in the range of from 1:5 to 1:1, preferably above 1:3 or 1:2 or even 1:1.5 or 1:1.2 or 1:1.1.

**Surfactant**

The cleaning composition of the invention comprises from 0.05% to 30% by weight of one or more surfactant(s). Preferably, the cleaning composition comprises from 0.1% to 25% of surfactant, typically from 0.5% to 20%, or from 1% to 15% by weight of surfactant. The surfactant may be anionic, nonionic and/or cationic. The substituted starch of the invention is particularly efficient in the presence of anionic surfactant.

The weight ratio of substituted starch to surfactant may be in the range of from 1:100 to 1:3, in particular from 1:50 to 1:5, or from 1:40 to 1:10, or from 1:30 to 1:20.

The weight ratio of substituted starch to anionic surfactant may be in the range of from 1:100 to 1:3, in particular from 1:50 to 1:5, or from 1:40 to 1:10, or from 1:30 to 1:20.

The weight ratio of nonionic surfactant to anionic surfactant may be in the range of from 1:100 to 1:1, in particular from 1:50 to 1:5, for example below 1:10 or 1:20.

**Anionic surfactant**

The cleaning composition of the invention may comprise from 0.05% to 30% by weight of one or more anionic surfactant. The cleaning composition may comprise 0.1% to 25%, in particular from 0.5% to 20% or from 1% to 18%, or even from 1.5% to 16% or from 2% to 14% by weight of anionic surfactant.

In particular, the anionic surfactant may comprise anionic surfactants selected from alkyl ester sulfonate(s); linear, branched, and modified alkylbenzene sulfonate(s); C10-C18 alkyl alkoxy sulfates; C10-C18 primary, branched-chain and random alkyl sulfates; C6-O-C18 secondary (2,3) alkyl sulfates; C10-C18 alkyl alkoxy carboxylate(s); fatty acid(s); mid-chain branched alkyl sulfate(s); mid-chain branched alkyl alkoxy sulfate(s); alpha-olefin sulfonate(s); phosphate ester(s); and mixtures thereof.
The anionic surfactant may comprise surfactant chosen among sarcosinate surfactants, isethionate surfactants and taurate surfactants. Preferred for use herein are alkali metal or ammonium salts of these surfactants. Most preferred herein are the sodium and potassium salts of the following: lauroyl sarcosinate, myristoyl sarcosinate, palmitoyl sarcosinate, stearoyl sarcosinate and oleoyl sarcosinate.

Non-ionic surfactant

The cleaning composition may comprise non-ionic surfactant. Where present the non-ionic detersive surfactant(s) is generally present in amounts of from 0.01wt% to 20wt%, or from 0.1wt% to 4wt% by weight of the cleaning composition.

The non-ionic detersive surfactant can be selected from the group consisting of: alkyl polyglycoside and/or an alkyl alkoxylated alcohol; C_{12-18} alkly ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C_{6-12} alkyl phenol alkoxylates wherein the alkoxylate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C_{12-18} alcohol and C_{6-12} alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C_{14-22} mid-chain branched alcohols, BA, as described in more detail in US 6,150,322; C_{14-22} mid-chain branched alkyl alkoxylates, BAEx, wherein x = from 1 to 30, as described in more detail in US 6,153,577, US 6,020,303 and US 6,093,856; alkylpolysaccharides as described in more detail in US 4,565,647, specifically alkylpolyglycosides as described in more detail in US 4,483,780 and US 4,483,779; polyhydroxy fatty acid amides as described in more detail in US 5,332,528, WO 92/06162, WO 93/19146, WO 93/19038, and WO 94/09099; ether capped poly(oxyalkylated) alcohol surfactants as described in more detail in US 6,482,994 and WO 01/42408; and mixtures thereof.

Cationic detersive surfactant

The cleaning composition may comprise a cationic detersive surfactant. When present, preferably the cleaning composition comprises from 0.01wt% to 10 wt%, or from 0.1wt% to 2wt% cationic detersive surfactant.

Suitable cationic detersive surfactants are alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, and alkyl ternary sulphonium compounds. The cationic detersive surfactant can be selected from the group consisting of: alkoxylate quaternary ammonium (AQA) surfactants as described in more detail in US 6,136,769; dimethyl hydroxyethyl quaternary ammonium surfactants as described in more detail in US 6,004,922; polyamine cationic surfactants as described in more detail in WO 98/35002, WO 98/35003, WO 98/35004, WO 98/35005, and WO 98/35006; cationic ester
surfactants as described in more detail in US 4,228,042, US 4,239,660, US 4,260,529 and US 6,022,844; amino surfactants as described in more detail in US 6,221,825 and WO 00/47708, specifically amido propyldimethyl amine; and mixtures thereof.

cationic detersive surfactants may be chosen among mono-Cg-io alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-Cio-12 alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-Cio alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride. Cationic surfactants such as Praepagen HY (tradename Clariant) may be useful and may also be useful as a suds booster.

**Builder**

The cleaning composition of the invention may comprise a builder. When a builder is used, the cleaning composition will typically comprise from 1% to about 40%, typically from 2 to 20%, or even from about 4% to about 15%, or from 5 to 10% by weight of builder(s).

The composition may further comprise from 1% to about 40%, typically from 2 to 20%, or even from about 4% to about 15%, or from 5 to 10% by weight of builder(s), chelant(s), or, in general, any material which will remove calcium ions from solution by, for example, sequestration, complexation, precipitation or ion exchange.

The composition may comprise a chelant. Suitable chelants include diethylene triamine pentaacetaetate, diethylene triamine penta(methyl phosphonic acid), ethylene diamine-N'N'-disuccinic acid, ethylene diamine tetraacetate, ethylene diamine tetra(methylene phosphonic acid) and hydroxyethane di(methylene phosphonic acid). A preferred chelant is ethylene diamine-N'N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP).

Preferably the ethylene diamine-N'N'-disuccinic acid is in S'S' enantiomeric form. The composition of the invention may comprise less than 3% or less than 2% or 1% or 0.5% of each of the above mentioned chelants.

Builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates, alkali metal silicates, layered silicates, such as SKS-6 of Clariant®, alkaline earth and alkali metal carbonates, aluminosilicate builders, such as zeolite, and polycarboxylate compounds, ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethylxysuccinic acid, fatty acids, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, citric acid,
oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxy succinic acid, and soluble salts thereof.

The cleaning composition may comprise less than 50%, in particular less than 25% or less than 20%, 15%, 10%, or 5% by weight of phosphate and/or aluminosilicate builders.

The cleaning composition may comprise from 0 to 50%, in particular from 1% to 25%, or less than 20%, or less than 15%, or less than 10%, or less than 5%, or less than 1% by weight of phosphate builder(s).

The cleaning composition may comprise from 0 to 50%, in particular from 1% to 25%, or less than 20%, or less than 15%, or less than 10%, or less than 5%, or less than 1% by weight of aluminosilicate builder(s). The aluminosilicate builder may comprise zeolite.

The cleaning composition may comprise from 0 to 50%, in particular from 1% to 25%, or less than 20%, or less than 15%, or less than 10%, or less than 5%, or less than 1% by weight of polycarboxylic acid(s) and salt(s) thereof.

The cleaning composition may comprise from 0 to 50%, in particular from 1% to 25%, or less than 20%, or less than 15%, or less than 10%, or less than 5%, or less than 1% by weight of layered silicate(s).

The cleaning compositions of the present invention may comprise from 0 to 50%, in particular from 1% to 25%, or less than 20%, or less than 15%, or less than 10%, or less than 5%, or less than 1% by weight of sodium carbonate.

**Adjunct ingredient**

The cleaning composition may comprise one or more adjunct ingredient(s). The precise nature of these additional adjunct components, and levels of incorporation thereof, will depend on the physical form of the composition and the nature of the operation for which it is to be used.

For example when the composition is a fabric care composition, suitable adjunct materials include, but are not limited to flocculating aid, chelating agents, dye transfer inhibitors, enzymes, enzyme stabilizers, catalytic materials, bleach activators, hydrogen peroxide, sources of hydrogen peroxide, preformed peracids, polymeric dispersing agents, clay soil removal/anti-redemption agents, brighteners, suds suppressors, dyes, perfumes, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids, and/or pigments. In addition to the disclosure below, suitable examples of such other adjuncts and levels of use are found in U.S. Patent Nos. 5,576,282, 6,306,812 B1 and 6,326,348 B1.
The cleaning composition may also comprise, in particular when the cleaning composition is an oral care composition, Anticalculus Agent, Fluoride Source, Thickening Agents, Flavoring and Sweetening Agents, and/or antimicrobial agents.

Preferably, the cleaning composition of the invention contains less than 3%, preferably up to 1%, and most preferably less than 0.1% or less than 0.01% or 0.001% or even 0.0001% of suds suppressor selected from the group consisting of trimethyl-, diethyl-, dipropyl-, dibutyl-, methylethyl-, phenylmethyl polysiloxane, and mixtures thereof. Preferably, the compositions of the invention contain less than 3%, preferably up to 1%, and most preferably less than 0.1% or less than 0.01% or 0.001% or even 0.0001% of suds suppressor.

**Cleaning composition**

The cleaning composition may be in any liquid or solid form, in the form of gel, paste, dispersion, preferably a colloidal dispersion or any combination thereof. The cleaning composition is preferably in a solid form or in the form of a paste. The cleaning composition may be in particulate form, for example in free-flowing particulate form. The composition in solid form can be in the form of an agglomerate, granule, flake, extrudate, bar, tablet or any combination thereof.

The cleaning composition may be capable of cleaning and/or softening fabric during a laundering process. The cleaning composition may be an oral care composition. The Oral care composition may be in the form of a toothpaste, dentifrice, tooth powder, tooth gel, subgingival gel, mouthrinse, denture product, mouthspray, lozenge, oral tablet, or chewing gum. The oral composition may also be incorporated onto strips or films for direct application or attachment to oral surfaces. The cleaning composition may be a hair care, or a dish care composition.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

The following examples are given by way of illustration only and therefore should not be construed to limit the scope of the invention.
EXAMPLES

Example 1: Oral care composition

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Function</th>
<th>1A</th>
<th>1B</th>
<th>1C</th>
<th>1D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica, dental type</td>
<td>Abrasive (cleaning agent)</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>NaF USP</td>
<td>Fluoride source for anticaries benefit</td>
<td>0.243</td>
<td>0.243</td>
<td>0.243</td>
<td>0.243</td>
</tr>
<tr>
<td>Sodium dodecyl phosphate (30% soln)</td>
<td>Anionic surfactant with functional properties</td>
<td>-</td>
<td>5.0</td>
<td>5.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Zinc citrate</td>
<td>Antimicrobial</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium acid pyrophosphate</td>
<td>Antitartar agent</td>
<td>4.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium saccharin</td>
<td>Sweetener</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>NaOH (50% soln)</td>
<td>pH adjuster</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>CMC sodium</td>
<td>Thickener</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>Opacifier</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Carboner 956</td>
<td>Thickener</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Flavor</td>
<td>Flavor</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Sodium lauryl sulfate (28% soln)</td>
<td>Main surfactant for foaming</td>
<td>4.0</td>
<td>4.0</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>Cocamidopropyl Betaine (30% soln.)</td>
<td>Co-surfactant for foaming</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sorbitol solution</td>
<td>Humectant and Carrier (vehicle)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Hydroxy Butyl Starch (MW 2,812 kDa, DS 0.066)</td>
<td>Foam Stabilizer</td>
<td>0.80</td>
<td></td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Sulfonated Starch (MW 47 kDa, DS 0.001)</td>
<td>Foam Stabilizer</td>
<td></td>
<td>0.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxy Methyl Starch with low DS of Quat (MW 80,000 kDa, DS 0.44)</td>
<td>Foam Stabilizer</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FD&amp;C Blue #1</td>
<td>Visual</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>USP Water</td>
<td>Carrier (vehicle)</td>
<td>Q.S</td>
<td>Q.S</td>
<td>Q.S</td>
<td>Q.S</td>
</tr>
</tbody>
</table>
Exemple 2: Fabric care compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>Example 2A</th>
<th>Example 2B</th>
<th>Example 2C</th>
<th>Example 2D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium LAS</td>
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What is claimed is:

1. A cleaning composition comprising from 0.05% to 30% by weight of surfactant and from 0.01% to 10% by weight of substituted starch, wherein the substituted starch has:
   - a total degree of substitution in the range of from 0.001 to 0.6,
   - a degree of substitution of anionic substituent in the range of from 0.001 to 0.04 and/or a degree of substitution of nonionic substituent in the range of from 0.01 to 0.5,
   - a degree of substitution of cationic substituent in the range of from 0 to 0.004,
   - an average per weight molecular weight in the range of from 10 000 to 100 000 000 Daltons.

2. A cleaning composition according to claim 1, comprising from 0.1% to 25% by weight of surfactant, in particular from 0.5% to 20%, or from 1% to 15% by weight of surfactant.

3. A cleaning composition according to any one of the preceding claims, comprising from 0.1% to 7% by weight of surfactant, in particular from 0.1% to 5%, or from 0.3% to 3% by weight of substituted starch.

4. A cleaning composition according to any one of the preceding claims, wherein the weight ratio of substituted starch to surfactant is in the range of from 1:100 to 1:3, in particular from 1:50 to 1:5, or from 1:40 to 1:10, or from 1:30 to 1:20.

5. A cleaning composition according to any one of the preceding claims, comprising less than 50%, in particular less than 25% or less than 20%, 15%, 10%, or 5% by weight of phosphate and/or aluminosilicate builders.

6. A cleaning composition according to any one of the preceding claims, wherein the substituted starch comprises substituted polymers selected from polymers of general formula:
and mixtures thereof, wherein each \( R \) is \( H \) or a substituent selected from the group of anionic substituent, nonionic substituent, and cationic substituent, wherein at least 70% by number of the \( R \) are \( H \), the degree of substitution of anionic substituent is in the range of from 0 to 0.04, the degree of substitution of nonionic substituent is in the range of from 0 to 0.5, the degree of substitution of cationic substituent is in the range of from 0 to 0.004, wherein either the degree of substitution of anionic substituent is of at least 0.002 or the degree of substitution of non-ionic is of at least 0.02, wherein \( n \) is such that said suds boosting substituted polymer(s) has an average per weight molecular weight ranging from 20 000 Daltons to 100 000 000 Daltons.

7. A cleaning composition according to any one of the preceding claims, wherein the substituted starch has:
   - a degree of substitution of anionic substituent in the range of from 0.001 and 0.04,
   - a degree of substitution of cationic substituent below the degree of substitution of anionic substituent,
   - an average per weight molecular weight in the range of from 20 000 to 500 000 Daltons.

8. A cleaning composition according to claim 7, wherein the substituted starch has a degree of substitution of anionic substituent comprising a sulphate or sulphonate group in the range of from 0.001 and 0.04.
9. A cleaning composition according to any one of the preceding claims, wherein the substituted starch has:
   - a degree of substitution of nonionic substituent in the range of from 0.01 and 0.5,
   - a degree of substitution of cationic substituent in the range of from 0 to 0.0009,
   - an average per weight molecular weight in the range of from 20 000 and 50 000 000 Daltons.

10. A cleaning composition according to claim 9, wherein the substituted starch has a degree of substitution of nonionic hydroxyalkyl substituent in the range of from 0.01 and 0.5.

11. A cleaning composition according to any one of the preceding claims, comprising less than 3%, in particular less than 1% or less than 0.1% of suds suppressor.

12. A cleaning composition according to any one of the preceding claims, being a fabric care product selected from the group consisting of liquid laundry detergents, solid laundry detergents, laundry soap products, laundry spray treatment products, or a dish washing detergent, a beauty care detergent, a shampoo, an oral care composition, or a household cleaning detergent.

13. A cleaning composition according to any one of the preceding claims being in the form of a paste or a solid.

14. A cleaning composition according to any one of the preceding claims being a fabric care or an oral care composition.

15. Use of a substituted starch, wherein the substituted starch has:
   - a total degree of substitution in the range of from 0.001 and 0.6,
   - a degree of substitution of anionic substituent in the range of from 0.001 and 0.04 and/or a degree of substitution of nonionic substituent in the range of from 0.01 and 0.5,
   - a degree of substitution of cationic substituent in the range of from 0 to 0.004,
   - an average per weight molecular weight in the range of from 10 000 to 100 000 000 Daltons,

   to increase the quantity of suds that can be generated by a cleaning composition.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C11D3/22 A61Q11/00 A61K8/73 C11D3/00  

According to International Patent Classification (IPC), or to both national classification and IPC.

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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| X        | GB 699 530 A (SCHOLTEN CHEMISCHE FAB)  
11 November 1953 (1953-11-11)  
page 2, line 63 - line 80; claims  
1, 6, 7, 13; examples 1, 3-5 | 1-3, 5-9, 11-15 |
| X        | EP 1 801 194 A1 (AJINOMOTO KK [JP])  
paragraphs [0006], [0 14], [0 17], [0 22], [0 23], [254]; claims 1, 8;  
examples 1, 3; tables 1-4 | 1-2, 4-7, 9, 11-15 |
| X        | EP 1 120 104 A1 (OREAL [FR])  
1 August 2001 (2001-08-01)  
paragraphs [0007], [0 17], [0 30], [0 73], [0 79], [0 82], [0 85]; claim 21;  
examples; table 1 | 1-2, 4-7, 11-13, 15 |

* Further documents are listed in the continuation of Box C  

X See patent family annex

* Special categories of cited documents

A: document defining the general state of the art which is not considered to be of particular relevance  
E: earlier document but published on or after the international filing date  
L: document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
O: document referring to an oral disclosure, use, exhibition or other means  
P: document published prior to the international filing date but later than the priority date claimed  
T: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
X: document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
Y: document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
Z: document member of the same patent family

Date of the actual completion of the international search  
15 January 2010

Date of mailing of the international search report  
22/01/2010

Name and mailing address of the ISA/  
European Patent Office, P B 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel (+31-70) 340-2Q00  
Fax (+31-70) 340-3016

Authorized officer  
Loi sel et-Tai sne, S
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<td>US 6 248 338 B1 (MUELLER WILFRIED [DE] ET AL) 19 June 2001 (2001-06-19) column 2, line 40 - column 3, line 29; claims 1-3,8-10, 25; example 46</td>
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<td>WO 2006/117071 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]; GIBBS C) 9 November 2006 (2006-11-09) claims 1, 9,13, 19; examples 3B p.41, 44</td>
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## INTERNATIONAL SEARCH REPORT

Information on patent family members

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