

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 832 964 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**01.04.1998 Bulletin 1998/14**

(51) Int. Cl.<sup>6</sup>: **C11D 1/65**

(21) Application number: **96870120.1**

(22) Date of filing: **19.09.1996**

(84) Designated Contracting States:  
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE**  
Designated Extension States:  
**AL LT LV SI**

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(54) **Liquid stable thickened cleaning compositions**

(57) The invention relates to stable thickened liquid compositions comprising a C12-C18 alkyl sulphonate or C12-C18 alkyl aryl sulphonate and from 0.1% to 15% by weight of the total composition of a quaternary ammonium surfactant, at a weight ratio of said quaternary ammonium surfactant to said sulphonate of 10 to 25. The compositions are particularly suitable for the cleaning of non-horizontal surfaces.

**EP 0 832 964 A1**

## Description

### Technical Field

5 The present invention relates to liquid self-thickened compositions for cleaning hard surfaces. More particularly, the present invention relates to stable acidic thickened liquid compositions typically comprising a source of active oxygen. These compositions find particular application in the cleaning of inclined hard-surfaces, such as toilet bowls and the like.

### Background of the Invention

10 It is well-known in the art that it is a desirable feature of a liquid hard surface cleaner that it should have a certain viscosity. Indeed, viscosity allows a more controlled handling, e.g., a more accurate dispensing of the product during use, as compared to a thinner product. Also, viscosity allows a better action of the product on inclined surfaces, such as toilets, bath tubs and the like, because viscosity prevents the product from running down inclined surfaces, like thinner liquids would. Preferably viscosity is built up by a so-called self-thickening system as opposed to using a thickener compound for that specific purpose. Indeed, thickeners, such as gums or polymers have at least one drawback that they affect the formula cost, while providing only one benefit, which is thickening. They do not participate to the actual cleaning of the surface and therefore represent "inert" materials. Also, some thickeners are detrimental to the physical and/or chemical stability of the products they are formulated in.

20 Also, there are some drawbacks associated with product viscosity. And a main drawback is that viscous products are typically difficult to rinse away because they have a good cling onto surfaces and because current self-thickening systems lead to the formation of stable foams. Thus, viscosity and ease of rinsing are somewhat conflicting requirements, but both are desirable in a single product for cleaning hard surfaces.

25 It is thus an object of the present invention to provide a liquid thickened composition which is viscous by means of a self-thickening system, and which is nevertheless easy to rinse away.

30 There are many such compositions known in the art that have the requisite viscosity characteristics. However, most of the self-thickening surfactant systems known in the art, whilst allowing to effectively increase the viscosity of liquid compositions, do have some disadvantages in use. Indeed, thickening surfactants like nonionic surfactants (nonyl phenol ethoxylates) or quaternary ammonium compounds have the disadvantage that they require to be used at high levels to achieve satisfactory viscosity, thus making their use expensive.

35 It is thus another object of the present invention to formulate liquid self-thickened compositions, especially liquid self-thickened acidic compositions, preferably comprising a source of active oxygen, having improved thickening properties at low total thickening surfactant level.

40 Also, some thickening surfactants show significant instability when formulated in liquid thickened compositions in the acidic pH range and typically in presence of a source of active oxygen, e.g., hydrogen peroxide, or a source thereof, like monopersulfate. This may also result in a loss of the total amount of active oxygen which would otherwise be available to perform bleaching action on the surface to be cleaned.

45 It is yet another object of the present invention to formulate liquid self-thickened compositions, especially liquid self-thickened acidic compositions typically comprising a source of active oxygen, which are physically and chemically stable for long storage periods.

50 It has now been found that by combining a quaternary ammonium surfactant and a C12-C18 alkyl sulphonate or C12-C18 alkyl aryl sulphonate at a weight ratio of said quaternary ammonium surfactant to said sulphonate of 10:1 to 25:1, improved thickening properties are delivered. In other words, it has unexpectedly been found that the addition of a small amount of a C12-C18 alkyl or C12-C18 alkyl aryl sulphonate to a quaternary ammonium surfactant, in a liquid composition, preferably a liquid acidic composition typically comprising a source of active oxygen, allows to formulate highly thickened compositions, as compared to the same composition without said C12-C18 alkyl sulphonate or C12-C18 alkyl aryl sulphonate, or to the same composition with a short chain alkyl or aryl sulphonate (e.g., xylene sulphonate), instead of said C12-C18 alkyl sulphonate or C12-C18 alkyl aryl sulphonate, as the thickening system.

55 Alternatively, the present invention allows to use low level of total thickening surfactant to achieve a given viscosity. In other words, to obtain a desired thickening effect for a given liquid composition, e.g., a given liquid acidic composition comprising a source of active oxygen, a lower level of total thickening surfactants (quaternary ammonium surfactants and C12-C18 alkyl and/or C12-C18 alkyl aryl sulphonate) is sufficient in the present invention, as compared to the level of quaternary ammonium surfactant which would otherwise be required to obtain the same thickening effect when used alone, in absence of any C12-C18 alkyl or C12-C18 alkyl aryl sulphonate, or as compared to the total level of quaternary ammonium surfactant and short chain alkyl or aryl sulphonate (e.g., xylene sulphonate) which would be required to obtain the same thickening. This thickening effect is even more noticeable in the most preferred compositions of the present invention wherein the source of active oxygen used is a persulfate salt such as monopersulfate salt. Indeed,

said persulfate salt further contributes to the thickening properties of the thickening system of the present invention.

The liquid thickened compositions according to the present invention exhibit excellent chemical and physical stability. For instance, in the embodiment of the present invention where the liquid thickened compositions of the present invention are formulated in the acidic pH range and further comprise a source of active oxygen, the decomposition of said source of active oxygen, e.g. persulfate salt, is reduced, as compared to the same compositions but with other surfactant blends, like for instance alkylethoxylated alcohols, instead of said quaternary ammonium surfactant and C12-C18 alkyl/alkyl aryl sulphonate.

A further advantage of the present invention is that the liquid thickened compositions herein are translucent, as opposed to clouded, and thus well accepted from a consumer view point. Also, the present invention allows to formulate compositions that are Newtonian. By "Newtonian" it is meant herein a composition which has the same viscosity whichever applied shear stress. An additional benefit derived from said compositions is that they are low foaming, both in the sense of the amount of foam initially generated during use, as well as in terms of foam stability. This benefit adds to the ease of rinsing benefit already obtained with the "mechanistic" benefit derived from the viscosity profile of the composition. Yet another benefit of the present invention is that this thickening system leads to excellent spreading and clinging on wet surfaces.

Another advantage of the present invention is that the compositions herein, and especially those acidic compositions typically comprising a source of active oxygen, are efficient on various surfaces to clean various soils and stains. Additionally, the preferred liquid thickened acidic compositions of the present invention when used to treat hard surfaces, especially toilet bowls, exhibit outstanding soil discoloration, soil solubilization and emulsification properties together with a germicidal action, this when used both in neat or diluted form.

A further advantage of the present invention is that the compositions herein are less sensitive to the presence of perfumes, whereas high levels of perfume are known to have a general tendency to significantly decrease composition viscosity by changing micellar aggregation.

#### Background art

EP-A-275 043 discloses an acidic cleaner for aluminum surfaces containing a peroxide, acids, a C12-C22 alkyl dimethylamine oxide. Said cleaner has a pH of at most 2. EP-A-275 043 discloses cationic surfactants as optional ingredients but no specific compounds of this class of surfactants are mentioned, let alone quaternary ammonium surfactants.

WO95/33024 discloses an aqueous viscous composition (pH = 0.5-7) comprising an amine oxide or amine and a secondary, or primary monobranched alkyl sulphate or sulphonate, a hydrotrope and an organic acid. No quaternary ammonium surfactants are disclosed.

GB 2071 688 discloses liquid acidic compositions comprising an inorganic acid and as a thickening agent a mixture of an amine or amine oxide with a cationic or nonionic surfactant. No anionic surfactants are disclosed.

US 3997 453 discloses a fabric softening composition comprising from 60% to 20% of a cationic quaternary ammonium softener and an anionic sulphonate, the weight ratio of cationic softener to anionic sulphonate being of from 40 to 5.

EP-A-720642 discloses compositions (having a viscosity of 40 cps to 4000 cps) comprising a viscosity decreasing short chain (C6-C10) surfactant and a viscosity restoring long chain surfactant mixture, i.e., a C12-C16 amine oxide and C12-C14 alkyl sulphate. However, no liquid thickened compositions comprising quaternary ammonium surfactants (a) and long chain alkyl/alkyl aryl sulphonates (C12-C18) (b) at a weight ratio of (a) to (b) of 10:1 to 25:1 are disclosed.

European patent application number 96870001.3 discloses perfumed acidic compositions having a pH below 2, a source of active oxygen, surfactants and a terpene/sesquiterpene perfume. Preferred compositions are thickened compositions comprising a quaternary ammonium surfactant and an amine oxide surfactant. Other surfactants like anionic alkyl or aryl sulphonates are disclosed therein. However, no thickened liquid compositions comprising quaternary ammonium surfactants (a) and long chain alkyl/alkyl aryl sulphonates (C12-C18) (b) at a weight ratio of (a) to (b) of 10:1 to 25:1 are disclosed.

EP-A-265 979 discloses acidic thickened aqueous cleaning compositions comprising a disinfecting and/or oxidizing agent, an organic anionic sulphonate selected from the group consisting of xylene sulphonate, cumene sulphonate and toluene sulphonate, and a surfactant selected from the group of (1) quaternary ammonium compounds wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group containing at least 12 carbon atoms and of (2) tertiary amine oxides wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group containing at least 16 carbon atoms. In contrast, the present invention uses quaternary ammonium surfactants together with long chain alkyl/alkyl aryl sulphonates (C12-C18) as the thickening system.

RD 30115 discloses thickened cleaning compositions displaying shear thinning behaviour. The thickeners comprise a fatty alkyl quaternary ammonium (e.g., hexadecyl trimethyl ammonium chloride) and a low-alkyl substituted arene sulphonate (e.g., sodium xylene sulphonate). This cleaning compositions may further comprise a disinfecting

agent like a hydroperoxide of formula ROOH wherein R= hydrogen or acyl may be present. The following composition is exemplified 1% of C16 trimethyl ammonium chloride, 0.9% of sodium xylene sulphonate, 3% of citric acid and 5% of hydrogen peroxide. No long chain alkyl/alkyl aryl sulphonates (C12-C18) are disclosed.

5 EP-A-188 025 discloses aqueous stable thickened low-pH bleaching compositions comprising an inorganic peroxy compound, a strong acid and a thickening surfactant. The compositions are said to have a viscosity of 10 to 250 mPa.s. The thickening surfactant is selected from (1) amine oxides wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group of C6 to C18 carbon atoms, preferably C12 to C18, (2) amines and (3) quaternary ammonium salts wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group of C8 to C18 carbon atoms. EP-A-188 025 teaches to use as a thickening surfactant one of these thickening surfactants. No C12-C18 alkylsulphonates or C12-C18 alkyl aryl sulphonates are disclosed, let alone liquid compositions comprising, as the thickening system, a quaternary ammonium surfactant together with a C12-C18 alkyl and/or C12-C18 alkyl aryl sulphonate at a weight ratio of quaternary ammonium surfactant to C12-C18 alkyl and/or C12-C18 alkyl aryl sulphonate of 10:1 to 25:1.

#### 15 Summary of the invention

The present invention encompasses a liquid thickened composition having a viscosity of more than 250 cps, when measured with a Carri-med rheometer at 50 dyne/cm<sup>2</sup> at 20°C, comprising a C12-C18 alkyl sulphonate or C12-C18 alkyl aryl sulphonate or mixtures thereof, and from 0.01% to 15% by weight of the total composition of a quaternary ammonium surfactant, at a weight ratio of said quaternary ammonium surfactant to said sulphonate of 10:1 to 25:1.

In a preferred embodiment of the present invention the liquid thickened compositions herein are acidic compositions, and in an even more preferred embodiment of the present invention said acidic compositions further comprise a source of active oxygen.

25 The present invention also encompasses a process of treating a hard-surface, especially a toilet bowl, wherein a liquid thickened composition according to the present invention, is applied in its neat or diluted form onto said surface, optionally left to act thereto for an effective period of time and then removed.

#### Detailed description of the invention

30 The compositions of the present invention comprise as an essential element a thickening system. Said thickening system comprises a quaternary ammonium surfactant, or mixtures thereof, together with a C12-C18 alkyl or C12-C18 alkyl aryl sulphonate, or mixtures thereof, at a weight ratio of quaternary ammonium surfactant to sulphonate of 10:1 to 25:1, preferably 11:1 to 20:1, more preferably 12:1 to 17:1 and most preferably 13:1 to 17:1.

35 Indeed, it has unexpectedly been found that by combining a quaternary ammonium surfactant with a C12-C18 alkyl sulphonate and/or a C12-C18 alkyl aryl sulphonate at a weight ratio of said quaternary ammonium surfactant to said sulphonate of 10:1 to 25:1, in an aqueous medium, a viscosity of more than 250 cps, when measured with a Carri-med rheometer at 50 dyne/cm<sup>2</sup> at 20°C, is obtained while exhibiting excellent physical and chemical stability. Alternatively, the present invention allows to use low level of total thickening surfactant to achieve a given viscosity.

40 The total level of thickening system, i.e., of quaternary ammonium surfactant and C12-C18 alkyl sulphonate and/or C12-C18 alkyl aryl sulphonate, to be used in a given liquid composition depends on the thickness desired for said composition, said level being lower than 20%, preferably between 1% and 10%, more preferably between 1% and 6%, and most preferably between 1% and 3.5%.

The compositions of the present invention have a viscosity of more than 250 cps at 20°C, preferably from 260 cps to 1500 cps, more preferably from 280 cps to 900 cps, and most preferably from 300 cps to 500 cps, when measured with a Carri-med rheometer CLS 100<sup>®</sup> by TA Instruments at 50 dyne/cm<sup>2</sup> with a 4 cm diameter cone spindle.

45 Suitable quaternary ammonium surfactants to be used according to the present invention are quaternary ammonium surfactants according to the formula R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>N<sup>+</sup>X<sup>-</sup>, wherein R<sub>1</sub> is a saturated or unsaturated, linear or branched alkyl, or aryl group of 1 to 30 carbon atoms, preferably of 10 to 25 carbon atoms, more preferably 12 to 20 carbon atoms and most preferably 14 to 18 carbon atoms, wherein R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups, and wherein X is selected from the group consisting of chloride, fluoride, methyl sulphate, methyl sulphonate, or hydroxide and the like. In the preferred embodiment of the present invention where a source of active oxygen like persulfate is present in the compositions herein the quaternary ammonium surfactant is preferably a non-chloride quaternary ammonium surfactant.

55 Particularly preferred to be used in the compositions of the present invention are trimethyl quaternary ammonium surfactants like myristyl trimethylammonium methyl sulphate, cetyl trimethylammonium methyl sulphate and/or tallow trimethylammonium methyl sulphate. Such trimethyl quaternary ammonium surfactants are commercially available from Hoechst, or from Albright & Wilson under the trade name EMPIGEN CM<sup>®</sup>.

The compositions according to the present invention comprise from 0.01% to 15% by weight of a quaternary ammonium surfactant, or mixtures thereof, preferably of from 0.1% to 10%, more preferably of from 0.5% to 5%.

Suitable C12-C18 alkyl sulphonates to be used herein include water-soluble salts or acids of the formula  $\text{RSO}_3\text{M}$  wherein R is a C<sub>12</sub>-C<sub>18</sub> linear or branched, saturated or unsaturated, alkyl group, preferably a C12-C16 alkyl group and more preferably a C14-C16 alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Suitable C12-C18 alkyl aryl sulphonates to be used herein include water-soluble salts or acids of the formula  $\text{RSO}_3\text{M}$  wherein R is an aryl, preferably a benzyl, substituted by a C12-C18 linear or branched saturated or unsaturated alkyl group, preferably a C12-C16 alkyl group and more preferably a C14-C16 alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Particularly suitable to be used herein are secondary C12-C18 alkyl or C12-C18 alkyl aryl sulphonates. By "secondary C12-C18 alkyl or C12-C18 alkyl aryl sulphonates" it is meant herein that in the formula as defined above, the  $\text{SO}_3\text{M}$  or aryl- $\text{SO}_3\text{M}$  group is linked to a carbon atom of the alkyl chain being placed between two other carbons of the said alkyl chain (secondary carbon atom).

An example of a C14-C16 alkyl sulphonate is Hostapur<sup>®</sup> SAS available from Hoechst. An example of commercially available alkyl aryl sulphonate is Lauryl aryl sulphonate from Su.Ma.

Depending on the end use envisioned, the compositions according to the present invention may further comprise a variety of other ingredients including other surfactants of all types to boost the performance over a wider range of soils/encrustations, acids, a source of active oxygen, bleach activators, organic or inorganic alkalis, dyes (like for example  $\alpha$  or  $\beta$  metal phthalocyanines), optical brighteners, builders, chelants, pigments, enzymes, dye transfer inhibitors, solvents, buffering agents, stabilizers and the like.

The liquid compositions according to the present invention are preferably aqueous compositions. Therefore, they comprise from 50% to 98% by weight of the total composition of water, preferably from 60% to 95% and more preferably from 70% to 90%. One of the achievements of the present invention is that the viscosity build up described hereinafter can be achieved with such a high amount of water, i.e., a small amount of actives.

In a preferred embodiment the liquid thickened compositions of the present invention are liquid thickened acidic compositions.

Accordingly, the compositions of the present invention are typically formulated at a pH between 0 to 7, preferably at a pH between 0 and 6, more preferably at a pH between 0 and 4, and most preferably at a pH between 0 and 2. Acidity contributes to formulate compositions according to the present invention which exhibit good limescale removing performance while having also good disinfecting properties. Also, in the embodiment of the present invention wherein the compositions herein further comprise a source of active oxygen, the acidic pH contributes to the chemical stability of said compositions. Accordingly, the compositions of the present invention further comprise organic and/or inorganic acids. Particularly suitable organic acids to be used herein are aryl and/or alkyl sulfonate, such as methane sulfonic acid or naphthalene disulfonic acid, citric acid, succinic acid, sulphamic acid, glutaric acid, adipic acid and the like. Particularly suitable inorganic acids are sulfuric acid, phosphoric acid, nitric acid and the like.

In a more preferred embodiment the compositions herein further comprise a source of active oxygen or mixture thereof. The source of active oxygen according to the present invention acts as an oxidizing agent, it increases the ability of the compositions to remove colored stains and organic stains in general, to destroy malodorous molecules and to kill germs. Suitable sources of active oxygen are hydrogen peroxide or sources thereof. As used herein a hydrogen peroxide source refers to any compound which produces perhydroxyl ions when said compound is in contact with water.

Suitable water-soluble inorganic sources of hydrogen peroxide for use herein include persulfates, percarbonates, perborates, persilicates, dialkylperoxides, diacylperoxides, performed percarboxylic acids, organic and inorganic peroxides and/or hydroperoxides and mixtures thereof.

Suitable organic peroxides/hydroperoxides include diacyl and dialkyl peroxides/hydroperoxides such as dibenzoyl peroxide, t-butyl hydroperoxide, dilauroyl peroxide, dicumyl peroxide, and mixtures thereof.

Suitable preformed peroxyacids for use in the compositions according to the present invention include diperoxydodecandioic acid DPDA, magnesium perphthalic acid, perlauric acid, perbenzoic acid, diperoxyazelaic acid and mixtures thereof.

Persulfate salts or mixtures thereof are the preferred sources of active oxygen to be used in the compositions according to the present invention. Preferred persulfate salt to be used herein is the monopersulfate triple salt. One example of monopersulfate salt commercially available is potassium monopersulfate commercialised by Peroxide Chemie GMBH under the trade name Curox<sup>®</sup>. Other persulfate salts such as dipersulfate salts commercially available

from Peroxide Chemie GMBH can be used in the compositions according to the present invention.

Persulfate salts are preferred to be used herein, as they allow when used together with the surfactant system of the present invention comprising a quaternary ammonium surfactant and a C12-C18 alkyl sulphonate and/or a C12-C18 alkyl aryl sulphonate to further increase the viscosity of a composition comprising them. Indeed, it is believed that the (HSO<sub>5</sub><sup>-</sup>) anions coming from the persulfate salt, like monopersulfate salt, strongly interact with the cationic head group of the quaternary ammonium surfactant displacing its own counterion (e.g., methylsulfate).

The compositions according to the present invention may comprise from 0.1% to 30% by weight of the total composition of a source of active oxygen, or mixtures thereof, preferably from 0.1% to 20%, and more preferably from 0.1% to 15%.

The compositions according to the present invention are chemically stable. By "chemically stable" it is for example meant herein that a composition comprising a source of active oxygen or mixtures thereof, such as persulfate salt, preferably does not undergo more than 40 % persulfate loss, in six months at room temperature (20°C-25°C). Persulfate concentration can be measured by back titration with potassium permanganate of a solution containing ammonium ferrous sulphate. Said stability test method is well-known in the art and is reported, for example, on the technical information sheet of Curox<sup>®</sup> commercially available from Interlox. Alternatively, persulfate concentration can also be measured using a chromatography method described in the literature for peracids (F. Di Furia et al., Gas-liquid Chromatography Method for Determination of Peracids, Analyst, Vol 113, May 1988, p 793-795).

The compositions according to the present invention are physically stable. By "physically stable" it is meant herein that the compositions of the present invention do not split in two or more phases when exposed in stressed conditions, e.g., at a temperature of 50 °C during 2 weeks.

In an embodiment of the present invention, the compositions as described hereinbefore further comprise a perfume or mixtures thereof. It is well-known that perfumes have a general tendency to significantly decrease the viscosity of compositions in which they are introduced. An advantage of the thickened compositions of the present invention, especially the acidic liquid thickened compositions that further comprise a source of active oxygen is, that they are less sensitive to the presence of perfume, even the presence of high levels of perfumes.

The perfume ingredients and compositions suitable to be used herein are the conventional ones known in the art. Suitable perfume compounds and compositions can be found in the art including U.S. Pat. Nos. : 4,145,184, Brain and Cummins, issued March 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,515,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979, all of said patents being incorporated herein by reference. In general, the degree of substantivity of a perfume is roughly proportional to the percentages of substantive perfume material used. Relatively substantive perfumes contain at least about 1%, preferably at least about 10%, substantive perfume materials. Substantive perfume materials are those odorous compounds that deposit on surfaces via the cleaning process and are detectable by people with normal olfactory acuity. Such materials typically have vapor pressures lower than that of the average perfume material. Also, they typically have molecular weights of about 200 and above, and are detectable at levels below those of the average perfume material. Perfume ingredients useful herein, along with their odor character, and their physical and chemical properties, such as boiling point and molecular weight, are given in "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969, incorporated herein by reference.

Examples of the highly volatile, low boiling, perfume ingredients are : anethole, benzaldehyde, benzyl acetate, benzyl alcohol, benzyl formate, iso-bornyl acetate, camphene, ciscitral (neral), citronellal, citronellol, citronellyl acetate, para-cymene, decanal, dihydrolinalool, dihydromyrcenol, dimethyl phenyl carbinol, eucaliptol, cedrol, geranial, geraniol, geranyl acetate, geranyl nitrile, cis-3-hexenyl acetate, hydroxycitronellal, d-limonene, linalool, linalool oxide, linalyl acetate, linalyl propionate, methyl anthranilate, alpha-methyl ionone, methyl nonyl acetaldehyde, methyl phenyl carbinyl acetate, laevo-menthyl acetate, menthone, iso-menthone, mycrene, myrcenyl acetate, myrcenol, nerol, neryl acetate, nonyl acetate, phenyl ethyl alcohol, alpha-pinene, beta-pinene, gamma-terpinene, alpha-terpineol, beta-terpineol, terpinyl acetate, and vertenex (para-tertiary-butyl cyclohexyl acetate). Some natural oils also contain large percentages of highly volatile perfume ingredients. For example, lavandin contains as major components : linalool; linalyl acetate; geraniol; and citronellol. Lemon oil and orange terpenes both contain about 95% of d-limonene.

Examples of moderately volatile perfume ingredients are : amyl cinnamic aldehyde, iso-amyl salicylate, beta-caryophyllene, cedrene, cinnamic alcohol, coumarin, dimethyl benzyl carbinyl acetate, ethyl vanillin, eugenol, iso-eugenol, flor acetate, heliotropine, 3-cis-hexenyl salicylate, hexyl salicylate, liliol (para-tertiarybutyl-alpha-methyl hydrocinnamic aldehyde), gamma-methyl ionone, nerolidol, patchouli alcohol, phenyl hexanol, beta-selinene, trichloromethyl phenyl carbinyl acetate, triethyl citrate, vanillin, and veratraldehyde. Cedarwood terpenes are composed mainly of alpha-cedrene, beta-cedrene, and other C15H24 sesquiterpenes.

Examples of the less volatile, high boiling, perfume ingredients are : benzophenone, benzyl salicylate, ethylene brassylate, galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gama-2-benzopyran), hexyl cinnamic aldehyde, lylal (4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-10-carboxaldehyde), methyl cedrylone, methyl dihydrojasmonate, methyl-beta-naphthyl ketone, musk indanone, musk ketone, musk tibetene, and phenylethyl phenyl acetate.

The compositions according to the present invention comprise up to 3% by weight of the total composition of a perfume or mixtures thereof, preferably of from 0.1% to 2% and more preferably of from 0.2% to 1%.

The compositions of the present invention may further comprise a chelating agent or mixtures thereof. Any chelating agents known to those skilled in the art are suitable to be used herein. Typically, such chelating agents include the ones selected from the group consisting of phosphonate chelating agents, amino carboxylate chelating agents, polyfunctionally-substituted aromatic chelating agents, and further chelating agents like glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid, and mixtures thereof. Chelating agents when used, are typically present herein in amounts ranging from 0.001% to 5% by weight of the total composition and preferably from 0.05% to 2% by weight.

Suitable phosphonate chelating agents to be used herein may include ethydrionic acid, metaphosphoric acid ( $\text{HPO}_3$ )<sub>n</sub>, pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ), methyldiene di phosphonic acid ( $\text{CH}_2(\text{H}_2\text{PO}_3)_2$ ), as well as amino phosphonate compounds, including aminotri(methylene phosphonic acid), amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonates. Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'- disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'- disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'-disuccinic acid is, for instance, commercially available under the trade-name ssEDDS® from Palmer Research Laboratories.

Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA), N- hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanoldiglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine diacetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS® and methyl glycine di-acetic acid (MGDA).

Particularly preferred chelating agents to be used herein are diethylene triamine methylene phosphonate, ethylene N,N'-disuccinic acid, diethylene triamine pentaacetate, aminotri(methylene phosphonic acid), glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid or mixtures thereof.

The compositions of the present invention may further comprise a radical scavenger or mixtures thereof. Any radical scavengers known to those skilled in the art are suitable to be used herein. Suitable radical scavengers for use herein include the well-known substituted mono and dihydroxy benzenes and their analogs, alkyl and aryl carboxylates and mixtures thereof. Preferred such radical scavengers for use herein include di-tert-butyl hydroxy toluene (BHT), hydroquinone, di-tert-butyl hydroquinone, mono-tert-butyl hydroquinone, tert-butyl-hydroxy anisole, benzoic acid, toluic acid, catechol, t-butyl catechol, benzylamine, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, n-propylgallate or mixtures thereof and highly preferred is di-tert-butyl hydroxy toluene. Radical scavengers when used, are typically present herein in amounts ranging from 0.001% to 2% by weight of the total composition and preferably from 0.001% to 0.5% by weight.

The present invention further encompasses a process of treating a hard-surface, especially inclined surfaces, wherein a composition according to the present invention is applied in its neat or diluted form onto said surface, optionally left to act thereto for an effective period of time and then removed for example by rinsing or flushing.

By "in its diluted form" it is meant herein that the compositions herein may be diluted with water up to 99% of water. Dilution may occur either before, after or while the composition is applied to a hard-surface.

The compositions herein find a preferred application in the cleaning of toilet bowls and bath tubs. In a preferred embodiment herein, the compositions of the present invention are applied neat onto the inclined surface, especially a toilet bowl, then left to act thereto typically for 1 minute to 1 hour, preferably 1 minute to 30 minutes and then removed by rinsing or flushing. In another embodiment herein, the compositions according to the present invention may be diluted while or after they are applied to the surface to be cleaned. For example, said compositions may be dispensed from a container neat onto said hard-surface, then diluted in water and left to act onto said surfaces for an effective period of time and then removed by rinsing or flushing.

As used in the foregoing paragraphs, the expression "treating" includes washing as the compositions used in the process according to the present invention comprise surfactants, optionally descaling limescale as said compositions may also be acidic, and optionally bleaching as said compositions may also comprise a source of active oxygen, pref-

erably hydrogen peroxide and/or persulfate salts. Preferably the three treatments are performed.

The compositions according to the present invention may be manufactured by adding the different ingredients in any order. However, the desired initial viscosity of an aqueous composition of the present invention is obtained immediately, when following a preferred mixing order for the incorporation of the different ingredients in said composition.

5 Accordingly, the present invention further encompasses a process for the manufacture of the liquid thickened compositions of the present invention, wherein said process comprises the steps of:

- preparing an aqueous medium comprising water and the source of active oxygen, if present, and the acid, if present,
- 10 - adding to said matrix the quaternary ammonium surfactant,
- then adding the perfume, if present, and finally the C12-C18 alkyl sulphonate and/or C12-C18 alkyl aryl sulpho-
- and as a final step the resulting composition is stirred at least one hour at 500 r.p.m. with a bladed stirrer at 20°C.

15 The present invention is further illustrated by the following examples.

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## Examples

Compositions are made which comprise the listed ingredients in the listed proportions (weight %).

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COMPOSITIONS (weight %)		I	II	III	IV	V	VI
Curox <sup>®</sup>		4	4	-	-	-	-
Hydrogen peroxide		-	-	3	3	3	3
Sulfuric acid		-	-	6	6	6	6
Naphtalen di sulphonic acid		8	8	-	-	-	-
C16 trimethyl ammonium sulphate		2.3	2.5	3.1	2.9	2.7	2.7
Lauryl aryl sulphonate		0.15	0.15	0.25	0.2	0.18	0.16
Hostapur SAS <sup>®</sup>		-	-	-	-	-	-
Perfume		0.4	0.4	0.4	0.4	0.4	0.4
water and minors	up to 100 %						
pH		0.5	0.5	0.5	0.5	0.5	0.5
Viscosity * (cps)		280	310	650	550	505	350
COMPOSITIONS (weight %)		VII	VIII	IX	X		
Curox <sup>®</sup>		-	4	4	4		
Hydrogen peroxide		3	-	-	-		
Sulfuric acid		6	6	6	6		
C16 trimethyl ammonium sulphate		2.6	1.8	2.5	2.3		
Lauryl aryl sulphonate		0.16	0.06	-	-		
Hostapur SAS <sup>®</sup>			-	0.15	0.12		
Perfume		0.4	0.4	0.4	0.4		
water and minors	up to 100 %						
pH		0.5	0.5	0.5	0.5		
Viscosity * (cps)		300	350	300	280		
Curox <sup>®</sup> is one of the commercial names of monopersulfate salts. Hostapur SAS <sup>®</sup> is a commercially available C14-C16 alkyl sulphonate.							

\*Viscosity grows with time; therefore, those are the lowest achievable viscosities with the above indicated compositions.

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The initial viscosity of the above compositions were measured by a Carri-Med Rheometer CLS 100 by TA instruments at fixed shear stress of 50 dyne/cm<sup>2</sup> at 20°C with a 4 cm diameter cone spindle. 50 dyne/cm<sup>2</sup> as shear stress value is representative of a fluid flow occurring on an inclined surface when the product thickness on the surface is about 1 mm and the only external force is due to the gravity field, as in a toilet cleaning application.

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All the above compositions according to the present invention are translucent, Newtonian compositions that provide significant benefits in toilet soils cleaning both when used neat or diluted. Said compositions are stable over long periods of time. Indeed, these compositions have not more than 10% available oxygen loss after 1 month at room temperature.

## Claims

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1. A liquid thickened composition having a viscosity of more than 250 cps, when measured with a Carri-med rheometer at 50 dyne/cm<sup>2</sup> at 20°C, comprising a C12-C18 alkyl sulphonate or C12-C18 alkyl aryl sulphonate, or mixtures thereof, and from 0.01% to 15% by weight of the total composition of a quaternary ammonium surfactant, at a

weight ratio of said quaternary ammonium surfactant to said sulphonate of 10:1 to 25:1.

2. A composition according to claim 1 wherein said quaternary ammonium surfactant is according to the formula  $R_1R_2R_3R_4N^+X^-$ , wherein  $R_1$  is a saturated or unsaturated, linear or branched alkyl, or aryl group of 1 to 30 carbon atoms, preferably of 10 to 25 carbon atoms, more preferably 12 to 20 carbon atoms and most preferably 14 to 18 carbon atoms, wherein  $R_2$ ,  $R_3$  and  $R_4$  are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups, and wherein X is selected from the group consisting of chloride, fluoride, methyl sulphate, methyl sulphonate, and hydroxide.
3. A composition according to any of the preceding claims wherein said C12-C18 alkyl sulphonate is a water-soluble salt or acid of the formula  $RSO_3M$  wherein R is a C<sub>12</sub>-C<sub>18</sub> linear or branched, saturated or unsaturated, alkyl group, preferably a C12-C16 alkyl group, and more preferably a C14-C16 alkyl group, and M is H or a cation, or ammonium or substituted ammonium, and/or wherein said C12-C18 alkyl aryl sulphonate is a water-soluble salt or acid of the formula  $RSO_3M$  wherein R is an aryl, preferably a benzyl, substituted by a C12-C18 linear or branched, saturated or unsaturated, alkyl group, preferably a C12-C16 alkyl group and more preferably a C14-C16 alkyl group, and M is H or a cation, or ammonium or substituted ammonium.
4. A composition according to any of the preceding claims wherein in said composition said quaternary ammonium surfactant and C12-C18 alkyl sulphonate and/or C12-C18 alkyl aryl sulphonate are present at a weight ratio of said quaternary ammonium surfactant to said sulphonate of 11:1 to 20:1, preferably of 12:1 to 17:1 and more preferably of 14:1 to 17:1.
5. A composition according to any of the preceding claims wherein the total level of said quaternary ammonium surfactant and said C12-C18 alkyl sulphonate and/or C12-C18 alkyl aryl sulphonate is no more than 20%, preferably between 1% to 10%, more preferably between 1% to 6% and most preferably between 1% to 3.5%.
6. A composition according to any of the preceding claims wherein said composition has a viscosity from 260 cps to 1500 cps, more preferably from 280 cps to 900 cps, and most preferably from 300 cps to 500 cps.
7. A composition according to any of the preceding claims wherein said composition is an acidic aqueous composition having a pH from 0 to 7, preferably from 0 to 6, more preferably from 0 to 4 and most preferably from 0 to 2.
8. A composition according to any of the preceding claims wherein said composition further comprises a source of active oxygen or mixtures thereof, preferably hydrogen peroxide and persulfate salts and more preferably monopersulfate.
9. A composition according to claim 8 wherein said source of active oxygen is present at a level of from 0.1% to 30% by weight of the total composition, preferably at a level of from 0.1% to 20%, and more preferably at a level of from 0.1% to 15%.
10. A composition according to any of the preceding claims wherein said composition further comprises a perfume, preferably at a level up to 3% by weight of the total composition, more preferably at a level of from 0.1% to 2% and most preferably at a level of from 0.2% to 1%.
11. A process of treating a hard-surface, preferably toilet bowl, wherein a composition according to any of the preceding claims is applied in its neat or diluted form onto said surface, optionally left to act thereto for an effective period of time, and then removed.
12. A process for the manufacture of a composition according to any of the claims 1 to 10, wherein said process comprises the steps of:
  - preparing an aqueous medium comprising water and, said source of active oxygen, if present, and an acid, if present,
  - adding to said matrix said quaternary ammonium surfactant,
  - then adding said perfume, if present, and finally said C12-C18 alkyl sulphonate and/or C12-C18 alkyl aryl sulphonate,
  - and as a final step stirring the resulting composition at least one hour at 500 r.p.m. with a bladed stirrer at 20°C.



European Patent  
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EUROPEAN SEARCH REPORT

Application Number  
EP 96 87 0120

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.6)
X	FR 2 526 441 A (COLGATE PALMOLIVE CO) * claims 1-4 *	1,2	C11D1/65
D,X	US 3 997 453 A (WIXON HAROLD E) * claims 1-4 *	1,2	
Y	EP 0 199 385 A (UNILEVER NV ET AL.) * column 1, line 25 - line 28 * * column 2, line 26 - line 30 * * column 3, last paragraph * * claims *	1,6-12	
Y	EP 0 606 712 A (CLOROX CO) * page 2, line 41 - line 45 * * page 6; example 3 * * claims 1-8,10-14 *	1,6-12	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
Place of search		Date of completion of the search	Examiner
BERLIN		27 January 1997	Pelli Wablat, B
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>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</p> <p>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                      .....                      &amp; : member of the same patent family, corresponding document</p>			

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