

(19)



(11)

**EP 3 040 408 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**06.07.2016 Bulletin 2016/27**

(51) Int Cl.:

**C11D 3/08** (2006.01)

**C11D 3/12** (2006.01)

**C11D 3/14** (2006.01)

**C11D 3/395** (2006.01)

**C11D 10/04** (2006.01)

**C11D 17/00** (2006.01)

(21) Application number: **14004460.3**

(22) Date of filing: **31.12.2014**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

**BA ME**

(71) Applicant: **Hayata Kimya Sanayi Anonim Sirketi  
41275 Kocaeli (TR)**

(72) Inventors:

- **Uzumcu, Murat  
Basiskele/Kocaeli (TR)**
- **Tas, Turgut  
Basiskele/Kocaeli (TR)**
- **Ergun, Ahmet  
Basiskele/Kocaeli (TR)**
- **Toslu, Nihat  
Basiskele/Kocaeli (TR)**
- **Acikalin, Korkut  
Basiskele/Kocaeli (TR)**

(54) **Aqueous liquid cleaning compositions comprising bleaching agent and abrasive particles**

(57) The present invention relates to the field of cleaning compositions, especially to cleaning compositions used in cleaning and/or scouring of hard surfaces. In particular, the present invention relates to liquid cleaning compositions comprising an abrasive material and a bleaching agent, whereby the cleaning compositions have the ability to stably suspend abrasive particles. The cleaning compositions of the present invention do not comprise any colloidal thickeners or any polymeric thickeners to suspend the abrasive particles stably in them-

selves. Cleaning compositions of the present invention stably suspend the abrasives with the aid of novel and specifically determined surfactant-electrolyte system wherein the cleaning compositions have specific electrical conductivity. Furthermore, the cleaning compositions of the present invention displays satisfactory bleach stability and contact time with vertical surfaces. The present invention also relates to a method of preparing said cleaning compositions.

**EP 3 040 408 A1**

**Description****FIELD OF THE INVENTION:**

5 [0001] The present invention relates to cleaning compositions. Particularly, the present invention relates to hard surface cleaning compositions. More particularly, the present invention relates to aqueous liquid cleaning compositions comprising abrasive particles and bleaching agent whereby the abrasive particles are stably suspended in said cleaning compositions.

10 [0002] The cleaning compositions of the present invention do not comprise any ingredient selected from polymeric thickeners, colloidal thickeners of alumina and clays, amine oxides as nonionic surfactants and amphoteric surfactants in order to suspend abrasive particles. The cleaning compositions of the present invention suspend the abrasive particles by comprising a specifically determined surfactant-electrolyte system and by having a specifically determined electrical conductivity. The cleaning compositions of the present invention stably suspend the abrasive particles without showing a physical phase separation and demonstrating almost constant viscosity values with time. Furthermore, the cleaning compositions of the present invention display satisfactory bleach stability and satisfactory contact time with vertical surfaces. The present invention also relates to a method of preparing said cleaning compositions.

**BACKGROUND OF THE INVENTION:**

20 [0003] Liquid cleaning compositions comprising abrasive particles and bleaching agent are known in the art. The abrasive particles are mainly used for cleaning of hard surfaces to remove hard stains or soils such as stubborn soils, greases, burnt-in materials, dried soils which are quite challenging to remove with the cleaning compositions that do not comprise abrasive particles. The abrasive particles make the removal of soils and stains easier by assisting the cleaning process physically. Moreover, addition of abrasive particles to compositions makes the compositions creamy-like which generally attract the consumers in a good sense. As for bleaching agents, their addition to cleaning compositions makes it possible to disinfect the cleaned surfaces as well as further assisting the soil and stain removal. These beneficial properties make abrasive particle and bleach agent comprising cleaning compositions desirable among the consumers.

25 [0004] On the other hand, in formulating the liquid cleaning compositions including abrasive particles and bleaching agent, there has been a particular problem of retaining the abrasive particles in suspension in the cleaning composition during the storage of the cleaning composition prior to use. The abrasive particles of the composition show a tendency to settle and pack at the bottom of the containers resulting in a physical phase separation. As a result of phase separation, the cleaning composition is needed to be shaken by consumer to maintain homogeneity prior to use. The shaking of cleaning composition is an additional step in cleaning process, and is not welcomed by most of the consumers since it is recognized as inconvenience. Besides, a simple shaking prior to use may not provide uniformity of cleaning composition, and may affect the cleaning performance negatively.

30 [0005] Another particular problem in said cleaning compositions is bleach stability which relates to the interactions between bleaching agents and the other ingredients of the cleaning composition, especially surfactants. The chemical interactions between bleaching agent and other ingredients can cause a degradation and loss of effectiveness of bleaching agents. As a result, the disinfection of cleaned surface may not be achieved or may be completed poorly, and the cleaning of bleach sensitive soils and stains may not be performed at a satisfactory level.

35 [0006] Another problem in said cleaning compositions is low cleaner composition-surface contact time in non-horizontal, especially in vertical surfaces. The said cleaning compositions are difficult to utilize on hard surfaces positioned vertically since they run along such surfaces quickly, thereby minimizing the contact time of cleaning composition with the said surface, which finally results in poor cleaning performance.

40 [0007] Numerous attempts have been made to overcome the problems given above.

45 [0008] US4599186A stated that a hard surface liquid abrasive scouring cleanser having bleach stability, substantial lack of phase separation and stable suspension of abrasives can be provided by a formulation comprising a colloidal aluminum oxide thickener, a bleach-stable amine oxide surfactant, an electrolyte/buffer in an amount sufficient to promote an environment in which surfactant and aluminum oxide can favorably associate, halogen bleach agent and particulate abrasive. Unfortunately, these hard surface compositions may become less flowable over time, and they still may require shaking prior to use. Moreover, adding colloidal thickeners to avoid settlement causes an increment in raw material and processing (storage, transportation etc.) costs, and requires an additional step in production process.

50 [0009] US5376297A, US5346641A are other examples of patents that use colloidal aluminum thickeners in abrasive hard surface cleaner formulations comprising bleach agent. Colloid-forming clays are other type of colloidal thickeners used in abrasive hard surface cleaning compositions comprising bleach agent. For instance, US4005027A claimed that an aqueous false body fluid hard-surface scouring cleanser having desirable chemical and physical stability could be obtained by a formulation comprising an inorganic colloid-forming clay selected from smectites, attapulgites or mixtures thereof, a bleaching agent which yields a hypochlorite species, a bleach-stable surfactant selected from water-soluble

alkyl sulfates containing 8-18 carbon atoms in alkyl group, particulate abrasive material, inorganic buffering agent, and deionized water.

[0010] US4235732A, US4051056A, GB1437857A are other patent examples which used colloidal-forming clays in their formulations. Unfortunately, clay comprising abrasive hard surface compositions have a known disadvantage of quick dry out, and may become less flowable over time, and, moreover, they still may require shaking prior to use. Moreover, adding any type of colloidal thickeners to avoid settlement causes an increment in raw material and processing (storage, transportation etc.) costs, and requires an additional step in production process.

[0011] Polymeric thickeners are another type of thickeners used in abrasive hard surface cleaning compositions comprising bleach agent.

[0012] For instance, EP0968272A1 claimed that the formulation comprising an alkali metal carboxylate, alkali metal salt, water dispersible non-ionic amine oxide, one or more water dispersible anionic sulphate or sulfonate surfactants, bleach releasing material such as alkali metal hypochlorite, pH adjusting agent, abrasive material, water and optionally detergency builder reduced the drawbacks of viscosity increase with storage time and poor flow properties. US4911857A stated that stably suspended abrasive particle containing formulation further comprised synthetic anionic detergent, soap, water soluble organic and/or inorganic salt other than phosphate, chlorine releasing bleaching agent and polyacrylate or polymethacrylate having a molecular weight between 500-3000. Other formulations comprising polymer thickener were given in US5470499A and US5348682A. The formulations comprising both polymeric thickener and colloidal thickener are also known in the art. For instance, US6268325B1 disclosed a composition comprising colloid-forming material, water-soluble polymeric thickener which together with colloid-forming material forms a thickening system, abrasive particles, a halogen based bleaching agent and water, in which abrasive particles were stably suspended. EP0892847B1 claimed a hard-surface scouring cleaner composition comprising abrasive particles, chlorine-containing bleach, a thickening system of cross-linked polyacrylate resin and synthetic smectite clay, bleach-stable surfactant system of one or more anionic surfactants, electrolyte/buffer and sodium or potassium hydroxide. Unfortunately, the compositions having polymeric thickeners have a disadvantage caused by the fact that hypochlorite bleach is destructive to most synthetic and natural thickeners. Although certain polyacrylates are somewhat less subject to degradation by hypochlorite bleach, many of these polymeric substances, particularly lower molecular weight polyacrylates, do not substantially increase viscosity. Moreover, adding polymeric thickeners causes an increment in raw material and processing (storage, transportation etc.) costs, and requires an additional step in production process.

[0013] In some of the previous practise, suspending capability of abrasives was provided by micellar interaction of electrolyte and surfactant. For instance, EP9942B1 asserted that a pourable scouring cleanser being capable of suspending abrasives comprises an anionic surfactant, a non-ionic surfactant such as amine oxide, chlorine-releasing bleaching agent such as sodium hypochlorite, whereby the total surfactant concentration is 0.1 to 0.5 moles/kg based on the total composition other than the abrasive. Amine oxide surfactants used in above mentioned example have good foaming properties, but, unfortunately, they may not be favourable in abrasive cleaners as the foam produced during the cleaning process reduces the scouring effect by forming a barrier between abrasive particles and cleaned surface. US4396525A disclosed a liquid scouring composition comprising an anionic surfactant, alkyl-amido betaine surfactant, abrasive, electrolyte, water and bleach as other ingredient. Unfortunately, alkyl-amido betaine surfactants are well known for their strength foaming properties which may result in poor scouring effect as the foam produced during the cleaning process forms a barrier between abrasive particles and cleaned surface.

[0014] There is still a great need for a hard-surface cleaning composition comprising abrasive particles and bleaching agent wherein the cleaning composition

(i) is capable of stably suspending the abrasive particles without forming a physical separation,

(ii) ensuring an almost constant viscosity with time,

(iii) demonstrates satisfactory bleach stability, and

(iv) discloses satisfactory contact time with vertical surfaces.

#### SUMMARY OF THE INVENTION:

[0015] Therefore, the main object of present invention is to provide an aqueous liquid hard surface abrasive bleaching cleaning composition free of polymeric thickeners, colloidal thickeners of alumina or clays, and any amphoteric surfactants or amine oxides, wherein the cleaning composition has the ability to stably suspend abrasive particles without disclosing any physical phase separation and disclosing an almost constant viscosity with time.

[0016] Further object of this invention is to provide an aqueous liquid hard surface abrasive bleaching cleaning composition which has satisfactory bleach stability in terms of bleach half-life.

[0017] Still further object of this invention is to provide an aqueous liquid hard surface abrasive bleaching cleaning composition which has a sufficient contact time on vertical surfaces.

[0018] The inventors of the present invention surprisingly found that a cleaning composition comprising specifically determined surfactant - electrolyte system and having a specifically determined electrical conductivity can provide the above targeted objects, such as bleach stability, stable abrasive suspension, almost constant viscosity and satisfactory contact time on vertical surfaces.

**DESCRIPTION OF DISCLOSURE:**

[0019] The inventors of the present invention surprisingly revealed that an aqueous hard surface cleaning composition having a pH value  $\geq 11.5$ , comprising:

(a) an anionic surfactant,

(b) a nonionic surfactant,

(c) a fatty acid soap,

(d) abrasive particles,

(e) a bleaching agent, and

(f) an electrolyte

can stably suspend the abrasive particles without disclosing a physical phase separation and maintain an almost constant viscosity with time characterized in that the electrical conductivity of said cleaning composition is less than 40 mS/cm. The said cleaning compositions also disclosed satisfactory bleach stability in terms of bleach half-life and an satisfactory contact time with vertical surfaces.

[0020] By "hard surface" it should be understood that the hard surfaces may include those found in bathrooms, kitchens, basements, garages etc. The hard surfaces may be tableware, kitchenware, bathware as well as floors and walls. The hard surfaces may be made up of any material such as marble, steel, aluminium, enamel, ceramic, porcelain, plastic excluding glass and polished parquet.

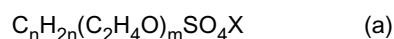
**SURFACTANTS**

[0021] Within the scope of present invention, the stable suspension of abrasive particles in cleaning compositions was provided by the micellar interactions between the surfactants and electrolyte which form a structured liquid capable of suspending abrasive particles. In order to achieve this structured liquid, the inventors found that a specific surfactant system composed of specific types and amounts of surfactants, a specific type and amount of electrolyte has to be provided.

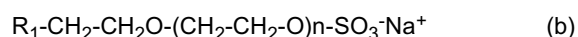
[0022] The cleaning compositions of the present invention comprise up to 10%, preferably up to 6% more preferably up to 3% total surfactant by weight of the total composition.

[0023] The anionic surfactant/nonionic surfactant ratio (by weight) of the present invention preferably changes between 1.5/1:5/1, more preferably changes between 2/1:3/1. Likely, the studies of present invention indicated that the total surfactant (anionic + nonionic) / electrolyte ratio (by weight) must be provided between 3.8/1:22/1, preferably between 5/1:15/1. Having provided these conditions, the inventors surprisingly noticed that the cleaning compositions have an electrical conductivity value of  $\leq 40$  mS/cm, preferably  $\leq 25$  mS/cm, more preferably  $\leq 15$  mS/cm, whereby the compositions of the present invention do not need any polymeric thickeners, colloidal thickeners of alumina or clays to form a structured liquid cleaning composition capable of suspending abrasive particles stably at the presence of bleaching agents.

[0024] The anionic surfactant of the present invention includes alcohol ethoxy sulphates. The structure of alcohol ethoxy sulphates (AES) can be described by the following formulas:



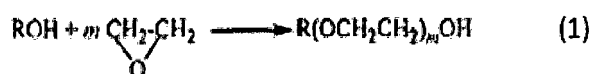
wherein  $n=12-18$ ,  $m \leq 8$  and X = sodium, ammonium or triethanolamine (TEA);



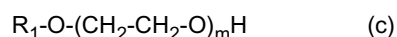
wherein  $R_1=C_{10}-C_{14}$  and  $n \leq 4$ .

[0025] The preferred anionic surfactant of the present invention is sodium lauryl ether sulphate (SLES) which falls into the category of formula (b). An aqueous concentrated SLES is derived from fatty alcohols by ethoxylation. The ethoxylation product is heterogeneous in the number of ethoxyl groups, where  $n$  in formula (b) is the mean or predominant ethoxyl group number (EO). The resulting ethoxylate is then converted to a half ester of sulphuric acid, which is then neutralized by conversion to sodium salt. The more preferred anionic surfactant of the present invention is sodium lauryl ether sulphate with a mean or predominant ethoxyl group number (EO) smaller than 2. The most preferred anionic surfactant of the present invention is sodium lauryl ether sulphate with a mean or predominant ethoxyl group number (EO)  $\leq 1$ . The cleaning composition of the present invention includes preferably 1-7%, more preferably 2-5.5% sodium lauryl ether sulphate by weight of the total composition. The non-limiting commercial sodium lauryl ether sulphate brands that can be found in the market are sulfochem™ from Lubrizol, SLES 70% from Recochem, EMAL from KAO, Texapon® from BASF and Hayat SLES from Hayat Kimya San. A.Ş.

[0026] The nonionic surfactant of the present invention includes alcohol ethoxylates which are very widely used surfactants in household cleaners owing to their desirable characteristics of rapid biodegradation, low to moderate foaming ability and tolerance of water hardness. Alcohol ethoxylates are obtained by addition of ethylene oxide to alcohol according to the following reaction (1):



[0027] The commonly used alcohols are primary  $C_8-C_{18}$  alcohols. The alcohols used as reactant in ethoxylation reaction may be synthetic, vegetable or animal originated. The synthetic alcohols may be Ziegler or Oxo alcohols. Ethoxylated alcohols represent mixtures of oligomer homologues with a wide ethylene oxide chain length distribution. Hence,  $m$  in reaction (1) is always some average (mean) or predominant value. The preferred nonionic surfactant of the present invention is shown by the formula (c):



wherein  $R_1$  = predominantly unbranched (linear)  $C_{13} - C_{15}$  oxo alcohol and  $m=3 - 11$ . The more preferred nonionic surfactant of the present invention is oxo alcohol ethoxylate wherein ethoxyl group number ( $m$ ) in formula (c) or in reaction (1) is predominantly 5 to 7. The cleaning composition of the present invention includes preferably 0.2-5%, more preferably 0.8-2% linear oxo alcohol ethoxylate by weight of the total composition. The non-limiting commercial alcohol ethoxylate brands that can be found in the market are Lutensol® from BASF, Emulsogen® and Genapol® from Clariant and Neodol from Shell.

[0028] The cleaning compositions of the present invention do not comprise any type of amine oxide surfactants as nonionic surfactants since their presence in cleaning compositions may lead to high sudsing/foaming during the cleaning process, and thus, decreases the cleaning performance by forming a barrier of foam/suds between the cleaned surface and the abrasive particles of the cleaning composition. The cleaning compositions of the present invention do not comprise any zwitter/amphoteric surfactant such as alkyl-amido betaines which are known to have good sudsing performance, especially when combined together with the anionic surfactants of alcohol ethoxy sulphates.

#### FATTY ACID SOAP

[0029] Fatty acid soap used according to the present invention promotes the suspension of abrasive particles in cleaning composition. The studies of the present invention indicated that the fatty acid soap amounts  $\leq 0.50$  % by weight of the total composition, preferably  $\leq 0.35$ % by weight of the total composition is high enough to promote the suspension of abrasive particles.

[0030] The fatty acid soap can be directly put to the cleaning compositions or can be produced during the cleaning composition preparation process. In present invention, the fatty acid soap was preferably produced during the preparation process by neutralizing the fatty acid with sodium hydroxide and/or sodium carbonate. The fatty acid neutralized may be palm fatty acid or coconut fatty acid. The preferable one is coconut fatty acid whose acid value and iodine value are between 253-263 mgKOH/g and 8-13 gI/100g, respectively.

[0031] The carbon weight distribution of preferred coconut fatty acid is  $\leq C_{10}$  max. 3%;  $C_{12}$  51-58%;  $C_{14}$  20-24%;  $C_{16}$  9-13%;  $C_{18}$  1-6%;  $C_{18:1}$  5-9%;  $C_{18:2}$  1-3%;  $\geq C_{18:2}$  max. 1%.

[0032] The fatty acid soap of the cleaning compositions of the present invention were produced from Palmera B1212 (KLK Oleo Company) fatty acid.

**[0033]** Palm kernel fatty acid used for neutralization may have an acid value and iodine value between 240-260 mgKOH/g and 14-23 g/100g, respectively. The carbon weight distribution of palm kernel fatty acid is  $\leq C_{10}$  max. 1.6%;  $C_{12}$  40-60%;  $C_{14}$  14-20%;  $C_{16}$  6-12%;  $C_{18}$  0-5%;  $C_{18:1}$  12-22%;  $C_{18:2}$  0-5%. The commercial palm kernel fatty acid may be found by KLK Oleo Company under the brand name of Palmera B1220.

#### ABRASIVE PARTICLES

**[0034]** Abrasive particles used according to present invention promote cleaning by providing a scouring action, in other words by assisting the cleaning action physically. Abrasive particles of the present invention can be insoluble or partially soluble or limitedly (poorly) soluble in water. The hardness of abrasive particles can be between 1 and 9 Moh's, preferably between 2 and 6 Moh's.

**[0035]** The abrasive particles can be selected from calcite, quartz, dolomite, feldspar, diatomaceous earth, talc, bentonite, pumice, pumicite, vermiculite, titanium dioxide, silica, silica sand, zirconium silicate, calcium silicate, whiting, tripoli, perlite, melamine granules, urea formaldehyde, polyurethane foam, poorly water soluble alkali metal carbonates such as calcium carbonate, agate, mica, garnet, kieselguhr, marble, volcanic ash, emery, flint, plastics such as polystyrene and polyacrylate, cellulosic or lignocellulosic particles obtained from biomasses such as pistachio shell, nut shell, almond shells, or any other plant originated particles. Mixtures of different types of abrasive particles can also be employed in the cleaning compositions to provide a balance composition having both hard and soft abrasives. The abrasive particle of the present invention is preferably calcite.

**[0036]** The abrasive particles can have a particle diameter between 0.1 to 250  $\mu\text{m}$ , preferably between 0.9 to 120  $\mu\text{m}$  wherein the average particle diameter is between 10-50  $\mu\text{m}$ , preferably between 20-40  $\mu\text{m}$ . The particle size distribution of the abrasive particles is preferably such that at least %70 by weight of particles have a diameter in the range of 1  $\mu\text{m}$  to 60  $\mu\text{m}$ .

**[0037]** The amount of abrasive particles included in cleaning compositions is preferably in the range of 30% to 70%, more preferably in the range of 40% to 60% by weight of the total composition.

#### BLEACHING AGENT

**[0038]** Bleaching agent used according to present invention makes it possible to disinfect the cleaned surface as well as further assisting soil and stain removal, especially removal of soils and stains which are sensitive to bleaching agents.

**[0039]** The bleaching agent of the present invention is the type of chlorine-releasing bleaching agent. Said bleaching agent can be alkali metal and alkaline earth metal hypochlorites, chloramines, chlorimines, chloramids, chlorimids. Specific examples are sodium hypochlorite, potassium hypochlorite, monobasic calcium hypochlorite, dibasic magnesium hypochlorite, potassium dichloroisocyanurate, sodium dichloroisocyanurate, sodium dichloroisocyanurate dehydrate, trichlorocyanuric acid, 1-3-dichloro-5-5-dimethylhydantoin, N-chlorosulfamide, Chloramine T, Dichloramine T, Chloramine B and Dichloramine B. The preferred bleaching agent of the present invention is sodium hypochlorite, NaClO, composed of sodium cation ( $\text{Na}^+$ ) and a hypochlorite anion ( $\text{ClO}^-$ ). The hypochlorite anion is a strong oxidizing agent and for this reason materials which yield this species are considered to be powerful bleaching agents.

**[0040]** Sodium hypochlorite used in the present invention was provided as aqueous solutions of 12% by weight. The concentration of aqueous solution containing hypochlorite ion was measured in terms of available (active) chlorine. The chlorine releasing bleaching agent can be present in the cleaning compositions of present invention in an amount sufficient to provide from 0.1% to 5%, preferably 0.5% to 2% available (active) chlorine. Conversion from % active chlorine (w/w) to % sodium hypochlorite (w/w) can be found by using equation (i):

$$\% \text{ sodium hypochlorite} = X \times 74.44 / 70.9 \quad (\text{i})$$

wherein X is sodium hypochlorite concentration as % active chlorine (w/w), 74.44 is sodium hypochlorite molecular weight and 70.9 is chlorine ( $\text{Cl}_2$ ) molecular weight. Thus, sodium hypochlorite can be present in the cleaning compositions of present invention in an amount from 0.1% to 5.5%, preferably 0.5% to 2.5% by weight of the total composition.

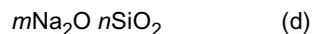
**[0041]** The pH of the cleaning composition is very important since chemical decomposition and hence loss of bleaching power becomes very significant at low pH values for hypochlorite containing solutions.

**[0042]** For this reason, the cleaning compositions must be buffered at pH's of above 11.5, preferably above 12.5, more preferably above 13.5.

## ELECTROLYTE

**[0043]** The inventors surprisingly found that if an appropriate surfactant mixture-electrolyte system and proper electrical conductivity is provided, liquid cleaning compositions can stably suspend abrasive particles at the presence of bleaching agents without needing any polymeric thickeners, colloidal thickeners of alumina or clays. By "electrolyte", it is meant the substances that dissolve in water to provide uni- or multivalent ions. Here, it is thought that if relative proportions of the anionic surfactant, nonionic surfactant and the electrolyte are provided in the cleaning composition, the interactions between the surfactants and electrolyte form a structured micellar configuration which is capable of suspending abrasive particles.

**[0044]** Appropriate electrolytes for the present invention are silicates, metasilicates, and polysilicates. The preferred electrolyte of the present invention is sodium silicate whose chemical composition can be expressed by the formula (d):



wherein the ratio  $n/m$  is referred to as the modulus of sodium silicate. The modulus of sodium silicate in present inventive cleaning compositions is preferably 3.75 to 1, more preferably 3 to 1.5, most preferably 2.2 to 1.8. The amount of sodium silicate in the present inventors cleaning compositions is from 0.1% to 5%, preferably 0.2% to 2% by weight of the total composition.

**[0045]** The studies of the present invention revealed that total surfactant / electrolyte (w/w) ratio must properly be set along with the electrical conductivity of the cleaning composition in order to stably suspend the abrasive particles within the cleaning composition at the presence of bleaching agent. The total surfactant / electrolyte ratio (w/w) must be between preferably 3.8/1 : 22/1, more preferably between 5/1 : 15/1. On the other hand, the electrical conductivity of the present inventive cleaning compositions must be less than 40 mS/cm, preferably less than 25 mS/cm, more preferably less than 15 mS/cm.

## OTHER INGREDIENTS

**[0046]** *Buffers/pH tuners:* Providing a high alkaline cleaning composition with a pH value >11.5, preferably >12.5, more preferably >13.5 is crucial in order to minimize chemical decomposition of hypochlorite yielding bleaching agent so that bleach stability can be maintained. Moreover, such alkaline pH values also favour cleaning effectiveness especially at the presence of oily and greasy soils and stains. The possible buffers/pH tuners that can be used in the scope of present invention are alkali metal carbonates, alkali metal bicarbonates and alkali metal hydroxides. Preferred buffers/pH tuners are sodium carbonate and sodium hydroxide. The inventive cleaning compositions of the present invention may comprise a single type or multi-type buffer/pH tuner types. The buffers/pH tuners can be used in cleaning compositions to set the pH of cleaning compositions to desired values. The cleaning compositions of the present invention may optionally comprise from 0.1% to 10%, preferably 0.2 to 5% buffers/pH tuners.

**[0047]** *Antifoam agents:* Antifoam agents can be used to prevent excess foaming (i) during the cleaning composition preparation (ii) during the filling of bottles with cleaning compositions in the manufacturing process and (ii) during the cleaning process applied by the consumers to the hard surfaces to remove the soils and/or stains. The preferred antifoam agent is silicone emulsion in which the emulsion comprises treated amorphous silica. Such a commercial product from Dow Corning Company (Dow Corning® DB-310) was used in the studies of present invention. The preferred amount of antifoam agent by weight of total composition is 0.001-0.5%.

**[0048]** *Perfume:* Perfume of any type (oil or encapsulated) can be added to cleaning compositions in order to provide a pleasant smell during and/or after the cleaning of soiled/stained surface by the consumer. The preferred amount of perfume by weight of total composition is 0.1-3%.

## PREPARATION OF CLEANING COMPOSITIONS

**[0049]** The cleaning compositions of the present invention were prepared by the following method:

1. Sodium carbonate is completely dissolved in deionized water at elevated temperatures of 50-90°C, preferably 70-80°C by mixing.

2. Fatty acid is introduced to the mixture, and is neutralized to produce fatty acid soap. Sodium hydroxide may optionally be added to complete the neutralization process.

3. Antifoaming agent is introduced to prevent excess foaming.

## EP 3 040 408 A1

4. Sodium silicate is added to the mixture when the mixture has the temperature of 20-60°C, preferably of 35-45°C.
5. Anionic surfactant is introduced to the mixture.
- 5 6. Nonionic surfactant is added to the mixture.
7. Abrasive particles are added to the mixture when the temperature of mixture is around 10-45°C, preferably 20-40°C, more preferably 25-35°C.
- 10 8. Bleaching agent is introduced to the mixture.
9. Finally, perfume is added.

15 **[0050]** During all of the stages of the preparation process, well and enough mixing of the mixture must be provided. It is important to prepare the cleaning composition in above order exactly, except that the order of the stages 4, 5 and 6 can be reorganized interchangeably without changing the order of other preparation stages. It is also important that the neutralization process must take place at around 70-80°C to complete the fatty acid soap production; the anionic and the nonionic surfactant must be added to the mixture below 60°C preferably below 45°C, and the bleaching agent and the perfume should not be added temperatures above 50°C, preferably 35°C. The preparation studies of the present  
20 invention indicated that a cleaning composition capable of stably suspending the abrasives without any physical phase separation and with an almost constant viscosity with time can be obtained if the conditions given above are provided.

### ANALYSIS and TEST METHODS

25 **[0051]** Viscosity: The viscosities of cleaning compositions were measured at 25°C by using a Brookfield viscometer (LVT) with spindle No. 2 at 12 rpm in a 150 ml sample. All of the results are average of three measurements. All of the viscosity values are in cP.

**[0052]** pH: The pH of the cleaning compositions were measured at 25°C by using Mettler Toledo Seven Easy pH meter. All of the results are average of three measurements.

30 **[0053]** Electrical conductivity: Electrical conductivity measurements were made by using WTW 330i conductivity meter at 25°C. All of the results are average of three measurements. All of the conductivity values are in mS/cm (milliSiemens/cm).

**[0054]** Active chlorine: Active chlorine analyses were done titrimetrically according to the TSE (Turkish Standarts Insitute) TS 3464 standart method. The standart method uses sodium thiosulfate as titrant. All of the active chlorine  
35 values are in weight percentage of total composition. All of the results are average of three measurements. The bleach stability was found satisfactory if the active chlorine amount of the cleaning composition did not fall below the half of the initial active chlorine value.

**[0055]** Stability test (for phase separation): Stability test of cleaning compositions with regard to phase separation was done by visual determination of physical phase separation in samples at 25°C for 8 weeks.

40 **[0056]** Viscosity test: The viscosity values of cleaning compositions were measured for 8 weeks. The viscosity test results were considered as almost constant if the viscosity change did not increase or decrease more than 5% of initial viscosity value. If the viscosity values did yield a viscosity change more than 5% of initial viscosity value then the viscosity values were recognized as variable, in other words not almost constant.

**[0057]** Vertical contact time test: Contact time tests were performed on ceramic surfaces of 10 cm x 10 cm dimension. 5 drops of cleaning compositions were dropped from Pasteur pipette on to the previously marked first spot of ceramic  
45 surface while the ceramic surface was horizontally positioned. Then, the ceramic surface was vertically positioned, and the time needed for cleaning composition to reach the previously marked second spot of ceramic surface which is 3 cm below the first spot was measured. All of the results are average of three tests. All of the values are in cm/sec. Smaller the value, better (longer) the contact time.

50 **[0058]** Cleaning performance test: The test soil was prepared by weighing the soil ingredients of 25% wt. butter, 25% wt. animal fat, 25% wt. margarine, 12.5% wt. ketchup and 12.5% mustard, and mixing these ingredients at 40-45°C under continuous mixing. Then, a roller was saturated with the prepared soil, and approximately 3 g of soil was distributed evenly to the white ceramic surfacecoverings. The soiled surfacecoverings were placed into a 180-185°C heated oven for 2 hours to simulate hard stains or soils such as stubborn soils, greases, burnt-in materials, dried soils which are quite  
55 challenging to remove with the cleaning compositions that do not comprise abrasive particles. The soiled surface coverings were cooled down to room temperature and were used in cleaning performance test.

**[0059]** The soiled ceramic surfacecoverings were cleaned by means of Ref 903 Wet Abrasion Scrub Tester (Sheen Instruments) with 15 double strokes using cut-to-size 9.2 cm x 4.2 cm cellulose type sponges at a pressure applied by

200 gr weight and a feed rate of 35 cm/s. The cleaning composition employed by Pasteur pipette was 20 drops.

**[0060]** The evaluation of cleaning performance was done by visual grading by three expert graders, and their grades were averaged. Three replicates of the tests were used, and the grades of all replicates were also averaged. The grading was done according to the Panel Score Unit (PSU) scale, defined as follows:

5

0 - There is no difference

1 - I think there is a difference

10

2 - I am sure there is a difference

3 - There is a large difference

15

4 - There is an extremely large difference

**[0061]** The grades were used with a "+" sign if the cleaning performance of the cleaning compositions according to the present invention were better than the compared cleaning compositions; and a "-" sign if the cleaning performance of the cleaning compositions according to the present invention were poorer than the compared cleaning compositions.

20

#### EXAMPLES

**[0062]** Exemplary, non-limiting embodiments of the present invention were given in Table 1 to provide a clear understanding. A person of ordinary skill in the art will recognize that other examples may be used without departing from the spirit and scope of the invention.

25

**[0063]** The examples 1, 2, 3, 5 and 8 which were prepared according to the present invention were found capable of stably suspending the abrasives since no physical phase separation were determined for 8 weeks after the preparation of cleaning compositions. Notice that, the electrical conductivities of the cleaning compositions that stably suspended the abrasives were below 40 mS/cm (Example 1 and 2).

30

**[0064]** On the other hand, the examples 4, 6, 7, 9, 10, 11, 12, 13, 14 which fall out of the scope of the present invention demonstrated physical phase separation.

35

40

45

50

55

Table 1. Examples (all of the components are % by weight)

Components / Examples	1	2	3	4	5	6	7
Anionic surfactant (Sodium lauryl ether sulfate 1EO - 70% wt.)	3.04	3.04	3.04	-	6.08	9.12	1.52
Anionic surfactant (Sodium lauryl ether sulfate 2EO - 70% wt.)	-	-	-	3.04	-	-	-
Nonionic surfactant (Linear alcohol oxo ethoxylate 5EO - 100% wt.)	0.84	0.84	-	0.84	1.68	2.52	0.42
Nonionic surfactant (Linear alcohol oxo ethoxylate 7EO - 100% wt.)	-	-	0.84	-	-	-	-
Fatty acid	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Sodium hydroxide - 50% wt.	0.40	0.40	-	-	-	-	-
Abrasive particle (Calcite)	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Sodium carbonate	4.25	4.25	4.00	4.00	4.00	4.00	4.00
Electrolyte (Sodium silicate - 45% wt.)	0.89	0.89	0.89	0.89	0.89	0.89	0.89
Bleaching agent (Sodium hypochlorite - 12% wt.)	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Anti-foaming agent (Silicone emulsion 5% wt.)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Perfume oil	0.30	-	0.30	0.30	0.30	0.30	0.30
Water	29.83	30.13	30.48	30.48	26.60	22.72	32.42
Stability test	S*	S	S	US**	S	US	US
Electrical Conductivity (mS/cm)	12.39	38.70	-	-	-	-	-

S\*: Stable, US\*\*: Unstable

Table 1. Examples (continued)

Components / Examples	8	9	10	11	12	13	14
Anionic surfactant (Sodium lauryl ether sulfate 1EO - 70% wt.)	3.04	3.04	3.04	3.04	1.52	-	3.04
Anionic surfactant (Sodium lauryl ether sulfate 2EO - 70% wt.)	-	-	-	-	-	-	-
Nonionic surfactant (Linear alcohol oxo ethoxylate 5EO - 100% wt.)	0.84	0.84	0.84	0.42	0.84	0.84	0.84
Nonionic surfactant (Linear alcohol oxo ethoxylate 7EO - 100% wt.)	-	-	-	-	-	-	-
Fatty acid	0.35	0.35	0.35	0.35	0.35	0.35	-
Sodium hydroxide - 50% wt.	0.40	-	-	-	-	0.40	-
Abrasive particle (Calcite)	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Sodium carbonate	4.25	4.00	4.00	4.00	4.00	4.25	4.25
Electrolyte (Sodium silicate - 45% wt.)	0.45	-	1.78	0.89	0.89	0.89	0.89
Bleaching agent (Sodium hypochlorite - 12% wt.)	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Anti-foaming agent (Silicone emulsion 5% wt.)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Perfume oil	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Water	30.28	31.37	29.59	30.90	32.00	32.87	30.58
Stability test	S	US	US	US	US	US	US
Electrical Conductivity (mS/cm)	14.12	-	-	-	-	110.50	-

[0065] For instance, Example 4 differed from the present invention since it did not comprise sodium lauryl ether sulphate having predominantly less than 2 ethoxyl groups and yielded phase separation. Example 4 clearly indicated that the type of anionic surfactant to be used in cleaning compositions has great importance.

[0066] On the other hand, Examples 6, 7 and 10 differed from the present invention since their sodium lauryl ether sulphate and linear oxo alcohol ethoxylate together to electrolyte ratios were out of the ratio range determined by the present invention. These examples revealed the cruciality of (anionic surfactant + nonionic surfactant) / electrolyte ratio.

[0067] Example 9 differed from the present invention since it did not comprise electrolyte, and proved the importance

of electrolyte availability.

[0068] Example 11 and 12 differed from the present invention since their sodium lauryl ether sulphate to linear oxo alcohol ethoxylate ratios were out of the ratio range specified by the present invention. This revealed the importance of anionic surfactant / nonionic surfactant ratio.

[0069] Example 13 differed from the present invention since it did not comprise anionic surfactant and had an electrical conductivity of app. 111 mS/cm which were out of the range specified by the present invention. This means that surfactant system is very important as well as the electrical conductivity. Finally, Example 14 differed from the present invention since it did not include any soap. This pointed that the presence of soap, although relevantly small amounts are sufficient, has great importance.

[0070] The viscosity and stability test results of Example 1 are given in Table 2. The results given Table 2 obviously supports that the cleaning composition prepared according to the present invention stably suspends the abrasive particles without yielding any physical phase separation and yielding almost constant viscosity. The highest viscosity change was observed as 1.85% which is smaller than 5%.

Table 2. Viscosity and Stability Test Results of Example 1.

	1. Week	2. Week	3. Week	4. Week	5. Week	6. Week	7. Week	8. Week
Viscosity values (cP)	1350	1325	1350	1375	1375	1375	1375	1375
Stability	S	S	S	S	S	SS	S	S

S=Stable, which means no physical phase separation was visually observed during the test period, and abrasive particles were successfully suspended.

[0071] The bleach stability test results of Example 1 are given in Table 3. The bleach stability of the cleaning composition prepared accordingly to the present invention showed satisfactory bleach stability since the active chlorine value did not fall below the half of initial active chlorine value during 8 week test period.

Table 3. Active Chlorine values (% wt.) of Example 1 (at 25°C)

	1. Week	2. Week	3. Week	4. Week	5. Week	6. Week	7. Week	Week
Example 1	1.01	0.99	0.97	0.91	0.88	0.85	0.72	0.55

[0072] Table 4 shows the vertical contact time test results of Example 1 of the present invention and a commercial aqueous abrasive cleaning composition comprising sodium hypochlorite. The vertical contact time value of commercial cleaning composition and Example 1 were essentially same. Thus, the vertical contact time results of Example 1 can be considered as satisfactory.

Table 4. Vertical contact time test results (all values are in cm/sec, smaller the value better the contact time)

	1. run	2. run	3. run	Average
Example 1	0.343	0.332	0.333	0.336
Commercial cleaning composition	0.321	0.331	0.329	0.327

[0073] Table 5 shows the cleaning performance test results wherein Example 1 was compared with a commercial aqueous abrasive cleaning composition comprising sodium hypochlorite. The positive signs in Table 5 prove that the cleaning performance of cleaning composition of present invention is slightly better than the cleaning performance of commercial aqueous abrasive cleaning composition comprising sodium hypochlorite. Note that, Example 1 was used in cleaning test after 2 months of its preparation.

Table 5. Cleaning performance test results (+ sign denotes that the cleaning performance of Example 1 is better than the cleaning performance of commercial cleaning composition)

	1. run	2. run	3. run	Average
Example 1 vs Commercial cleaning composition	+1	+1.33	+1.33	+1.22

[0074] Table 6 shows the cleaning performance test results wherein Example 1 was compared with Example 14 in which a physical phase separation was observed during the stability test. The positive signs in Table 6 obviously indicated that the cleaning performance of cleaning composition of present invention (Example 1) is better than the cleaning performance of phase forming cleaning composition (Example 14) which falls out of the scope of present invention. Note that, both Example 1 and Example 14 were used in cleaning test after 2 months of their preparation. Example 14 was shaken prior to cleaning test since it demonstrated phase separation.

Table 6. Cleaning performance test results (+ sign denotes that the cleaning performance of Example 1 is better than the cleaning performance of Example 14)

	1. run	2. run	3. run	Average
Example 1 vs Example 14	+2	+2	+2	+2

## Claims

1. An aqueous hard surface cleaning composition comprising,

- (g) an anionic surfactant,
- (h) a nonionic surfactant,
- (i) a fatty acid soap,
- (j) abrasive particles,
- (k) a bleaching agent, and
- (l) an electrolyte
- (m) water

**characterized in that** the electrical conductivity of said cleaning composition is less than 40 mS/cm, wherein said composition is capable of stably suspending abrasive particles and having a pH value of more than 11.5.

2. An aqueous hard surface cleaning composition according to claim 1 comprising,

- a) a sodium lauryl ether sulphate
- b) a linear oxo alcohol ethoxylate
- c) a fatty acid soap
- d) abrasive particles
- e) a chlorine releasing bleach agent
- f) silicate
- g) water

wherein at least 70% by weight of abrasive articles particle size is between 1 micrometer to 60 micrometer, preferably between 10 micrometer to 50 micrometer.

3. A cleaning composition according to claim 1 or claim 2, wherein the said cleaning composition does not comprise any ingredient selected from polymeric thickeners, colloidal thickeners of alumina, clays, amine oxides and amphoteric surfactants.

4. A cleaning composition according to preceding claims, wherein the electrical conductivity of said cleaning composition is less than 25 mS/cm, preferably less than 15mS/cm.

5. A cleaning composition according to claim 1 to claim 3, wherein the said anionic surfactant comprises sodium lauryl ether sulphate having predominantly less than 2 ethoxy groups.

6. A cleaning composition according to claim 1 to claim 3, wherein the said nonionic surfactant is linear oxo alcohol ethoxylate having predominantly 5 to 7 ethoxy groups.

7. A cleaning composition according to claim 1 to claim 3, wherein the said fatty acid soap is selected from palm fatty acid soap and/or coconut fatty acid soap and the said cleaning composition comprises less than or equal to 0.35% by weight of said fatty acid soap.

8. A cleaning composition according to claim 1 to claim 3, wherein the said electrolyte is sodium silicate, said bleaching agent is sodium hypochlorite and said abrasive particles are calcite.
- 5 9. A cleaning composition according to Claim 5 and 6, wherein the ratio of sodium lauryl ether sulphate and linear oxo alcohol ethoxylate together to electrolyte is between 3.8/1 : 22/1, preferably 5/1 : 15/1 by weight.
10. A cleaning composition according to Claim 5 and 6, wherein the ratio of sodium lauryl ether sulphate to linear oxo alcohol ethoxylate is between 1.5/1 : 5/1, preferably 2/1 : 3/1 by weight.
- 10 11. A cleaning composition according to preceding claims, wherein the cleaning composition comprises:
- (a) 1-7% of sodium lauryl ether sulphate predominantly has  $\leq$  one ethoxyl group
  - (b) 0.2-5% of linear oxo alcohol ethoxylate predominantly having 5 to 7 ethoxyl groups,
  - (c)  $\leq$  0.35% of fatty acid soap,
  - 15 (d) 30-70% calcite,
  - (e) 0.1-5.5 % sodium hypochlorite,
  - (f) 0.1-5% sodium silicate
  - (g) water
- 20 by weight of total composition.
12. A cleaning composition according to claim 11, wherein the cleaning composition comprises:
- (a) 2-5.5% of sodium lauryl ether sulphate predominantly has  $\leq$  one ethoxyl group,
  - 25 (b) 0.8-2% of linear oxo alcohol ethoxylate predominantly having 5 to 7 ethoxyl groups,
  - (c)  $\leq$  0.35% of fatty acid soap,
  - (d) 40-60% calcite ,
  - (e) 0.5-2.5% sodium hypochlorite,
  - (f) 0.2-2% sodium silicate
  - 30 (g) water
- by weight of total composition.
13. A cleaning composition according to Claim 12, wherein the cleaning composition comprises:
- 35 (a) 2-5.5% of sodium lauryl ether sulphate predominantly has  $\leq$  one ethoxyl group,
  - (b) 0.8-2% of linear oxo alcohol ethoxylate predominantly having 5 to 7 ethoxyl groups,
  - (c)  $\leq$  0.35% of fatty acid soap,
  - (d) 40-60% calcite,
  - 40 (e) 0.5-2.5% sodium hypochlorite,
  - (f) 0.2-2% sodium silicate,
  - (g) 0.001-0.5% antifoaming agent,
  - (h) 0.1-3% perfume
  - (i) optionally, 0.1-10% buffers/pH tuners
  - 45 (j) water
- by weight of total composition.
14. A preparation method of a cleaning composition according to any preceding claim comprising the stages of:
- 50 (i) neutralization of fatty acid with sodium carbonate in aqueous medium and optionally addition of sodium hydroxide to complete the neutralization
  - (ii) addition of antifoaming agent
  - (iii) addition of electrolyte to the mixture
  - 55 (iv) addition of anionic surfactant
  - (v) addition of nonionic surfactant
  - (vi) addition of abrasive particles
  - (vii) addition of bleaching agent

(viii) optionally addition of perfume

wherein the order of stages (iii), (iv) and (v) may be reorganized interchangeably without changing the order of other stages.

5

15. A preparation method of a cleaning composition according to claim 14 comprising the steps of:

10

(i) neutralization of fatty acid with sodium carbonate in aqueous medium at temperatures between 50-90°C, preferably 70-80°C and optionally addition of sodium hydroxide to complete the neutralization

(ii) addition of antifoaming agent

(iii) addition of electrolyte to the mixture at temperatures between 20-60°C, preferably 35-45°C

(iv) addition of anionic surfactant at temperatures below 60°C, preferably below 45°C

(v) addition of nonionic surfactant at temperatures below 60°C, preferably below 45°C

15

(vi) addition of abrasive particles at temperatures between 10-45°C preferably between 25-35°C

(vii) addition of bleaching agent at temperatures between 10-40°C preferably between 20-35°C

(viii) optionally addition of perfume at temperatures between 10-40°C preferably between 20-35°C.

**Amended claims in accordance with Rule 137(2) EPC.**

20

1. An aqueous hard surface cleaning composition comprising, an anionic surfactant,

(a) a nonionic surfactant,

(b) a fatty acid soap,

25

(c) abrasive particles,

(d) a bleaching agent,

(e) an electrolyte,

(f) water

30

**characterized in that** the electrical conductivity of said **cleaning** composition is less than 40 mS/cm, wherein said composition is capable of stably suspending abrasive particles and having a pH value of more than 11.5. comprise upto 10 % by weight total surfactant with an anionic to nonionic surfactant ratio of between 1.5/1 : 5/1 by weight and total surfactant (anionic + non-ionic)/electrolyte ratio of 3.8/1 : 22/1

35

whereas said hard surface **cleaning** composition is free of polymeric thickeners, colloidal thickeners of alumina or clays.

2. An aqueous hard surface **cleaning** composition according to claim 1 comprising,

a) a sodium lauryl ether sulphate having predominantly less than 2 ethoxy group

40

b) a linear oxo alcohol ethoxylate having predominantly 5 to 7 ethoxy groups

c) a fatty acid soap

d) abrasive particles

e) a chlorine releasing bleach agent

f) silicate

45

g) water

wherein at least 70% by weight of abrasive articles particle size is between 1 micrometer to 60 micrometer, preferably between 10 micrometer to 50 micrometer.

50

3. A **cleaning** composition according to preceding claims, wherein the electrical conductivity of said **cleaning** composition is less than 25 mS/cm, preferably less than 15mS/cm.

4. A **cleaning** composition according to preceding claims, wherein the **cleaning** composition comprises:

55

a) 1-7% of sodium lauryl ether sulphate predominantly has  $\leq$  one ethoxyl group

b) 0.2-5% of linear oxo alcohol ethoxylate predominantly having 5 to 7 ethoxyl groups,

c)  $\leq$  0.35% of fatty acid soap,

d) 30-70% calcite,

- e) 0.1-5.5 % sodium hypochlorite,
- f) 0.1-5% sodium silicate
- g) water

5 by weight of total composition.

5. A cleaning composition according to claim 4, wherein the cleaning composition comprises:

- 10 (a) 2-5.5% of sodium lauryl ether sulphate predominantly has  $\leq$  one ethoxyl group,
- (b) 0.8-2% of linear oxo alcohol ethoxylate predominantly having 5 to 7 ethoxyl groups,
- (c)  $\leq$  0.35% of fatty acid soap,
- (d) 40-60% calcite,
- (e) 0.5-2.5% sodium hypochlorite,
- (f) 0.2-2% sodium silicate
- 15 (g) water

by weight of total composition wherein,  
the ratio of sodium lauryl ether sulphate and linear oxo alcohol ethoxylate together to electrolyte is between 5/1 :  
15/1 by weight and  
20 the ratio of sodium lauryl ether sulphate to linear oxo alcohol ethoxylate is between 2/1 : 3/1 by weight.

25

30

35

40

45

50

55



EUROPEAN SEARCH REPORT

Application Number  
EP 14 00 4460

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	US 5 346 641 A (ARGO BRIAN P [US] ET AL) 13 September 1994 (1994-09-13) * column 1, lines 8-10; claims; examples * -----	1-15	INV. C11D3/08 C11D3/12 C11D3/14 C11D3/395 C11D10/04 C11D17/00
X	US 5 554 321 A (CHOY CLEMENT K [US] ET AL) 10 September 1996 (1996-09-10) * column 2, lines 9-15 * * column 8, lines 23-30 * * column 9, lines 26-54 * * claims; examples * -----	1-15	
X	EP 0 292 910 A2 (COLGATE PALMOLIVE CO [US]) 30 November 1988 (1988-11-30) * page 4, lines 9-44; claims; examples * -----	1-15	
X	US 2012/258904 A1 (BJELOPAVLIC MICK [US] ET AL) 11 October 2012 (2012-10-11) * paragraphs [0013], [0021], [0043], [0044], [0048], [0049], [0055]; claims; examples * -----	1-15	
A	EP 0 530 708 A2 (ALBRIGHT & WILSON [GB]) 10 March 1993 (1993-03-10) * page 11, lines 16-34; claims; examples * -----	1-15	TECHNICAL FIELDS SEARCHED (IPC) C11D
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 3 June 2015	Examiner Péntek, Eric
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

EPO FORM 1503 03/82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 14 00 4460

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03-06-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5346641	A	13-09-1994	NONE
US 5554321	A	10-09-1996	CA 2165668 A1 30-03-1995 DE 69427301 D1 28-06-2001 DE 69427301 T2 13-09-2001 EP 0720646 A1 10-07-1996 ES 2156900 T3 01-08-2001 US 5470499 A 28-11-1995 US 5554321 A 10-09-1996 WO 9508619 A1 30-03-1995
EP 0292910	A2	30-11-1988	AU 609482 B2 02-05-1991 AU 1666788 A 01-12-1988 CA 1315636 C 06-04-1993 DE 3852571 D1 09-02-1995 DE 3852571 T2 17-08-1995 DK 293188 A 29-11-1988 EP 0292910 A2 30-11-1988 NO 882339 A 29-11-1988
US 2012258904	A1	11-10-2012	US 2012258904 A1 11-10-2012 WO 2012138826 A2 11-10-2012
EP 0530708	A2	10-03-1993	AT 148158 T 15-02-1997 AU 665766 B2 18-01-1996 AU 2133092 A 11-03-1993 BG 61079 B1 31-10-1996 BG 96827 A 24-03-1994 BR 9203375 A 20-04-1993 CA 2077253 A1 01-03-1993 CN 1073973 A 07-07-1993 CZ 9202674 A3 12-05-1993 DE 69216955 D1 06-03-1997 DE 69216955 T2 12-06-1997 DZ 1616 A1 17-02-2002 EG 20081 A 31-05-1997 EP 0530708 A2 10-03-1993 ES 2099775 T3 01-06-1997 FI 923867 A 01-03-1993 HU 216618 B 28-07-1999 IL 102950 A 31-03-1996 IN 185580 A1 03-03-2001 JP 3193143 B2 30-07-2001 JP H05209198 A 20-08-1993 MA 22635 A1 01-04-1993 NO 923377 A 01-03-1993

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 14 00 4460

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03-06-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		NZ 244159 A	22-12-1994
		PL 295782 A1	23-08-1993
		RO 111203 B1	30-07-1996
		TN SN92077 A1	08-06-1993
		TR 27553 A	08-06-1995
-----			

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- US 4599186 A [0008]
- US 5376297 A [0009]
- US 5346641 A [0009]
- US 4005027 A [0009]
- US 4235732 A [0010]
- US 4051056 A [0010]
- GB 1437857 A [0010]
- EP 0968272 A1 [0012]
- US 4911857 A [0012]
- US 5470499 A [0012]
- US 5348682 A [0012]
- US 6268325 B1 [0012]
- EP 0892847 B1 [0012]
- EP 9942 B1 [0013]
- US 4396525 A [0013]