International Patent Classification:
- CUD 3/12 (2006.01)
- CUD 3/37 (2006.01)

International Application Number:
PCT/EP2013/074141

Filing Date:
19 November 2013 (19.1.2013)

Priority Data:
12195463.0 4 December 2012 (04.12.2012) EP

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Designated States (unless otherwise indicated, for every kind of national protection available):

Designated States (unless otherwise indicated, for every kind of regional protection available):

Declarations under Rule 4.17:
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(1)H)
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:
- with international search report (Art. 21(3))

Title: HARD SURFACE CLEANING COMPOSITION

Abstract:
Liquid hard surface cleaning composition comprising 10 to 95 wt. % of a liquid solvent; and 0.1 to 75 wt. % of a surfactant; and 5 to 60 wt. % of abrasive calcite particles; and 0.01 to 10 wt. % of polyethyleneimine: wherein the weight ratio of calcite particles to polyethyleneimine is from 1:1 to 500:1; wherein the pH of the liquid hard surface cleaning composition is at least 8. It was found that the liquid cleaning composition according to the invention provided an improved (next-time) cleaning efficiency of hard surfaces.
HARD SURFACE CLEANING COMPOSITION

TECHNICAL FIELD

This invention relates to a liquid hard surface cleaning composition comprising polyethylenimine and calcite particles and to a method for cleaning hard surfaces.

BACKGROUND

Many people spend a considerable amount of time and effort on cleaning of hard surfaces in or around the home or office on a regular basis. Examples of hard surfaces are table-tops, leather, ceramic tiles, dish surfaces and car-bodies.

To clean hard surfaces liquid cleaning compositions are typically used to improve cleaning efficiency (e.g. reduce the time and/or effort required).

Hard surface cleaning compositions can be diluted or in undiluted form, applied as a spray, or rubbed on using a cloth and any other convenient way. Sometimes a liquid cleaning composition may require rinsing from the surface after the cleaning. Hard surface cleaning compositions typically comprise surfactants, pH adjusters and abrasives to aid stain or soil removal.

For example, surfactants typically lower the surface tension of a liquid, the interfacial tension between two liquids and/or that between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. For example, abrasive particles typically improve the transfer of force from the cleaner to the stain/soil.

Hard surface cleaning compositions are known which provide a 'next-time' cleaning benefit. A next-time cleaning benefit is the observation that after treatment of the surface with such a composition, new stains/soils can be cleaned more efficiently.
US 3,810,846 discloses compositions for treating hard surfaces which renders such surfaces easier to clean, wherein the compositions comprise condensation products of a long-chain amine and a polyethylenimine or polyethylenoxy group or both.

However, there is a continued need for hard surface cleaning compositions which provide a further improved next-time cleaning benefit for hard surfaces (and thereby further reduce the time and/or effort required to remove stains/soils).

**SUMMARY OF THE INVENTION**

We have surprisingly found that a liquid hard surface cleaning composition comprising a certain ratio of polyethylenimine and calcite particles; and additionally a liquid solvent and surfactant provides an improved next-time cleaning benefit.

Accordingly, in a first aspect the invention relates to a liquid hard surface cleaning composition comprising

- 10 to 95 wt. % of a liquid solvent; and
- 0.1 to 75 wt. % of a surfactant; and
- 5 to 60 wt. % of abrasive calcite particles; and
- 0.01 to 10 wt. % of polyethylenimine;

wherein the weight ratio of calcite particles to polyethylenimine is from 1:1 to 500:1 and wherein the pH of the liquid hard surface cleaning composition is at least 8.

Without wishing to be bound by theory it is believed that the improved cleaning by the composition according to the invention is a result of balancing two opposing requirements. On the one hand, hard surface cleaning compositions require a relatively high amount of calcite particles to provide efficient cleaning. On the other hand a high amount of calcite particles may reduce the cleaning efficiency benefit provided by the polyethylenimine.

To clean a hard surface and provide a next-time cleaning benefit, the composition according to the invention is applied to the surface to be cleaned. Particularly good cleaning results were achieved when in the applied composition on the hard surface is
agitated by suitable means, such as by using a brush. Finally, the applied composition is preferably gently removed from the hard surface by rinsing and/or by an absorbent cloth.

Therefore in a further aspect the invention relates to a method for the cleaning of a hard surface comprising the following steps:

a) application of the liquid composition according to the invention to the hard surface;
b) agitation of the applied composition on the hard surface;
c) optionally gently removing the visible liquid composition by rinsing, by use of a cloth or both.

DETAILED DESCRIPTION OF THE INVENTION

In the context of the present invention, the terms "soil" and "stain" as used herein generally comprise all kinds of soils and stains generally encountered in the household, either of organic or inorganic origin, whether visible or invisible to the naked eye, including soiling solid debris and/or with bacteria or other pathogens. The term 'soil' includes stubborn soil, which means strongly adhering soils that are typically very difficult to remove, such as burnt-on and/or baked-on food residues. Weight percentage (wt. %) is based on the total weight of the composition unless otherwise stated. Throughout this specification, all stated viscosities are those measured at a shear rate of 20 s⁻¹ and at a temperature of 25°C unless stated to be otherwise. This shear rate is the shear rate that is usually exerted on the liquid when poured from a bottle. The liquid detergent compositions according to the invention are shear-thinning liquids.

By hard surface is meant any kind of surface typically found in and around home or office houses like kitchens, bathrooms, e.g., floors, walls, tiles, windows, cupboards, sinks, showers, shower plastified curtains, wash basins, WCs, fixtures and fittings and the like made of different materials like ceramic, vinyl, no-wax vinyl, linoleum, melamine, glass, Inox, Formica, vitroceramic, any plastics, plastified wood, metal or any painted or varnished or sealed surface and the like. Home or office hard surfaces also include household appliances including, but not limited to refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens,
dishwashers and so on. Such hard surfaces may be found both in private households as well as in commercial, institutional and industrial environments. Home or office hard surfaces include dish surfaces. With dish surfaces is meant herein dishes, glasses, pots, pans, baking dishes and flatware made from ceramic, china, metal, glass, plastic (polyethylene, polypropylene, polystyrene, etc.), wood, enamel, Inox, Teflon, or any other material commonly used in the making of articles used for eating and/or cooking.

An improved cleaning efficiency (i.e. 'an improved cleaning') indicates that the removal of soil and/or stains from a hard surface requires less time and/or effort (e.g. force exerted by the user). For example when less swiping actions are needed to remove a stain/soil from a hard surface using about the same force, the cleaning efficiency is improved. For example, in case the same number of swiping actions is required, but less force needs be applied, the cleaning efficiency is improved. Clearly, an improved cleaning may also be indicated by a similar effort to remove an increased amount of soil/stain. It will be appreciated that some stains/soils type are harder to remove than others, and that to compare cleaning efficiency preferably a comparison is made using the cleaning of the same type of stain/soil.

**Polyethylenimine.**

The polyethylenimine according to the invention preferably contains from 6 to 20,000 repeating units. Mixtures may be used. Preferably the polyethylenimine comprises at least 5%, more preferably at least 10% and even more preferably at least 20% of tertiary amine functions. The polymers may be linear or branched homopolymers or copolymers, or homopolymers or copolymers of dendrimer structure.

Preferably the polyethylenimine according to the invention are essentially not alkoxylated, such as ethoxylated and/or propoxylated.

Polyethylenimines according to the invention preferably have the following general formula:
Wherein represents an integer ranging from 6 to 20000, preferably from 8 to 2500.

These polymers are generally terminated with amine end functions and especially primary amines.

Preferably the polyethylenimine according to the invention has an average molecular weight of 10,000 to 5,000,000; preferably from 50,000 to 2,000,000; more preferably from 100,000 to 1,500,000 and even more preferably from 500,000 to 1,000,000 Dalton.

Molecular weights may be measured by quasi-elastic light scattering.

Preferably the polyethylenimine according to the invention has an average cationic charge density from 5 to 35 meq/g, more preferably from 10 to 30 meq/g and even more preferably from 15 to 25 meq/g and still even more preferably from 18 to 22 meq/g.

Charge density may be measured by the Kjeldahl method or calculated.

Preferably the liquid cleaning composition according to the invention comprises polyethylenimine in an amount of from 0.02 to 5 wt. %, more preferably from 0.04 to 2 wt. %, even more preferably from 0.06 to 1 wt. % and still even more preferably from 0.08 to 0.5 wt. %.

Suitable polyethylenimine according to the invention is commercially available, for example under the trade name 'Lupasol FG' or 'Lupasol PS' (Supplier: BASF). Preferably the polyethylenimine according to the invention is Lupasol FG or Lupasol PS and more preferred is Lupasol PS.

Abrasive calcite particles
Preferably the amount of calcite particles in the liquid hard surface cleaning composition according to the invention is from 6 to 50 wt. %, more preferably from 7 to 40 wt. %, even more preferably from 8 to 30 wt. % and still even more preferably from 9 to 25 wt. %.
It will be appreciated that the average particle size of the calcium particles is not excessively large or excessively small to provide good cleaning efficiency. For example on the one hand, a calcite population with an excessively large particle size (e.g. above 2000 micron (µm)), add little to the cleaning as having a small surface to weight ratio and would require very high particle load in the composition to be effective. In addition, excessively large particle are too easily detected visually or provide bad tactile experience while handling. For example, on the other hand, a calcite population with an excessively small particle size (e.g. below 0.1 µm) are not desirable as these may be hard to remove from the hard surface leaving the surface with a visible residue.

It was observed that a certain average size of the calcite particles improves the cleaning efficiency of the liquid composition according to the invention. Preferably the mean volume average size of the calcite particles is from 0.1 to 500 µm, more preferably from 1 to 250 µm, even more preferably from 5 to 150 µm, still even more preferably from 10 to 75 µm and still even more preferably from 25 to 70 µm.

The average particle size may be measured using techniques and equipment known in the art (e.g. using sieve analysis). Preferably a Malvern Mastersizer X (Malvern Instruments, Worcestershire, UK) is used to measure particle size, operated according to supplier instructions.

Abrasive calcite particles of suitable size can be made from calcium carbonate, for example by mechanical grinding followed by suitable size sorting methods such as sieving. Furthermore abrasive calcite particles of a range of average particle sizes are commercially available. For example Calcium particles with a mean particle size of 35 µm are available under the trade name Omyacarb 30 - AV (Supplier: Omya Greater South, Milano, Italy).

Preferably the calcite particles have sharp edges and an average a particle has at least one edge or surface having concave curvature. More preferably, the particles herein have a multitude of sharp edges and each particle has at least one edge or surface having concave curvature. The sharp edges of the particles are defined by edges having a tip.
radius below 20 pm, preferably below 8 pm, most preferably below 5 pm. The tip radius is defined by the diameter of an imaginary circle fitting the curvature of the edge extremity.

**Ratio**

Preferably the liquid hard surface cleaning composition according to the invention comprises a ratio of calcite particles: polyethylenimine from 10:1 to 400:1, more preferably from 20:1 to 300:1, even more preferably from 30:1 to 200:1, still even more preferably from 35:1 to 150:1, still even more preferably from 40:1 to 125:1 and still even more preferably from 45:1 to 75:1. In particular, more preferred ratio's have an improved next-time cleaning benefit.

**Surfactants**

The liquid cleaning composition according to the invention preferably comprise from 0.1 to 75 wt. % of surfactant.

Said surfactant (detergent active) is generally chosen from anionic and nonionic detergent actives. The cleaning composition may further or alternatively comprise cationic, amphoteric and zwitterionic surfactants.

Preferably the liquid hard surface cleaning composition according to the invention comprises from 1 to 50 wt. %, more preferably from 2 to 25 wt. % and even more preferably from 3 to 10 wt. % of surfactant.

Preferably the liquid hard surface cleaning composition according to the invention comprises surfactant which comprises for at least 50 wt. % more preferably 75 wt. % and still even more preferably at least 95 wt. % of anionic surfactant, based on the total amount of surfactant.

Preferably liquid hard surface cleaning composition according to the invention has a surfactant:polyethylenimine ratio of from 1:1 to 100:1, more preferably from 5:1 to 75:1, even more preferably from 10:1 to 50:1 and still even more from 20:1 to 35:1.
Suitable synthetic (non-soap) anionic surfactants are water-soluble salts of organic sulphuric acid mono-esters and sulphonic acids which have in the molecular structure a branched or straight chain alkyi group containing from 6 to 22 carbon atoms in the alkyi part.

Examples of such anionic surfactants are water soluble salts of:

- (primary) long chain (e.g. 6-22 C-atoms) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;
- alkyi benzene sulphonates, such as those in which the alkyi group contains from 6 to 20 carbon atoms;
- secondary alkanesulphonates;
and mixtures thereof.

Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;
- sulphates of ethoxylated aliphatic alcohols containing 1-12 ethyleneoxy groups;
- alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which the alkyi groups contain from 4 to 14 carbon atoms;
- the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali,
and mixtures thereof.

The preferred water-soluble synthetic anionic surfactants are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of alkyl-benzenesulphonates and mixtures with olefinsulphonates and alkyi sulphates, and the fatty acid mono-glyceride sulphates.

The most preferred anionic surfactants are alkyl-aromatic sulphonates such as alkylbenzenesulphonates containing from 6 to 20 carbon atoms in the alkyi group in a straight or branched chain, particular examples of which are sodium salts of
alkylbenzenesulphonates or of alkyl-toluene-, xylene- or phenolsulphonates, alkylnaphthalene-sulphonates, ammonium diamylnaphthalene-sulphonate, and sodium dinonyl-naphthalene-sulphonate.

If synthetic anionic surfactant is to be employed the amount present in the cleaning compositions of the invention will generally be at least 0.1 wt. %, preferably at least 0.5 wt. %, more preferably at least 1.0 wt. %, but not more than 20 wt. %, preferably at most 10 wt. % and more preferably not more than 5 wt. %.

A suitable class of nonionic surfactants can be broadly described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive hydrogen atom. The length of the hydrophilic or polyoxyalkylene chain which is attached to any particular hydrophobic group can be readily adjusted to yield a compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB. Particular examples include:

- the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol/ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol;
- condensates of alkylphenols having C6-C15 alkyl groups with 5 to 25 moles of ethylene oxide per mole of alkylphenol;
- condensates of the reaction product of ethylene-diamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000.

Other classes of nonionic surfactants are:

- tertiary amine oxides of structure $R_1R_2R_3N-0$, where $R_1$ is an alkyl group of 8 to 20 carbon atoms and $R_2$ and $R_3$ are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure $R_1R_2R_3P-0$, where $R_1$ is an alkyl group of 8 to 20 carbon atoms and $R_2$ and $R_3$ are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
dialkyl sulphoxides of structure R₁R₂S=O, where R₁ is an alkyl group of from 10 to 18 carbon atoms and R₂ is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;

- fatty acid alkylolamides, such as the ethanol amides;
- alkylenoxide condensates of fatty acid alkylolamides;
- alkyl mercaptans.

If nonionic surfactant is to be employed the amount present in the cleaning compositions of the invention will generally be at least 0.1 wt. %, preferably at least 0.5 wt. %, more preferably at least 1.0 wt. %, but not more than 20 wt. %, preferably at most 10 wt. % and more preferably not more than 5 wt. %.

It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in said compositions.

Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulphonate and sodium N₂-hydroxy-dodecyl-N-methyltaurate.

Examples of suitable cationic surfactants can be found among quaternary ammonium salts having one or two alkyl or aralkyl groups of from 8 to 20 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethylammonium chloride.

A specific group of surfactants are the tertiary amines obtained by condensation of ethylene and/or propylene oxide with long chain aliphatic amines. The compounds behave like nonionic surfactants in alkaline medium and like cationic surfactants in acid medium.

Examples of suitable zwitterionic surfactants can be found among derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic
water-solubilising group, for instance betaine and betaine derivatives such as alkyl betaine, in particular C12-C16 alkyl betaine, 3-(N,N-dimethyl-N-hexadecylammonium)-propane 1-sulphonate betaine, 3-(dodecylmethyl-sulphonium)-propane-1-sulphonate betaine, 3-(cetylmethyl-phosphonium)-propane-1-sulphonate betaine and N,N-dimethyl-N-dodecyl-glycine. Other well known betaines are the alkylamidopropyl betaines e.g. those wherein the alkylamido group is derived from coconut oil fatty acids.


Liquid solvent
The liquid hard surface cleaning composition according to the invention comprises 10 to 95 wt. % of a liquid solvent, which is preferably water, an organic solvent (e.g. ethanol, glycerol) or a combination thereof.

Preferably the composition comprises 35 to 92 wt. %, more preferably from 55 to 90 wt. % and even more preferably 65 to 85 wt. % of liquid solvent.

Preferably the composition according to the invention comprises at least 50 wt. %, more preferably at least 75 wt. %, even more preferably at least 85 wt. % and still more preferably at least 95 wt. % of water, based on the total weight of liquid solvent.

pH
The liquid hard surface cleaning composition according to the invention has a pH of at least 8.

It was found that at a pH below 8 the cleaning efficiency of the composition according to the invention is reduced.
Preferably the pH of the liquid composition according to the invention is at least 8.5, more preferably at least 9, even more preferably at least 9.5, still even more preferably at least 10, still even more preferably at least 10.5 and still even more preferably at least 11.

Preferably the liquid hard surface cleaning composition according to the invention has a pH of at most 13.

The pH of the cleaning composition used in the method of the invention may be adjusted with organic or inorganic acids or bases. Preferred inorganic bases are preferably alkali or alkaline earth hydroxides, ammonia, carbonates or bicarbonates, the alkali metal preferably being sodium or potassium or the alkaline earth metal preferably being calcium or magnesium. The organic bases are preferably amines, alkanolamines and other suitable amino compounds. Inorganic acids may include hydrochloric acid, sulphuric acid or phosphoric acid, and organic acids may include acetic acid, citric acid or formic acid as well as dicarboxylic acid mixtures such as Radimix (trademark, Radici Group) and Sokalan DCS (trademark, BASF).

Other optional ingredients
The composition according to the invention may include additional optional ingredients, which aid cleaning performance.

For example, in particular when the composition contains one or more anionic surfactants, the composition may preferably comprise detergent builders in an amount of more preferably from 0.1 to 25 wt.%. Suitable inorganic and organic builders are well known to those skilled in the art.

For example, the composition according to the invention may comprise a suds regulating material, which can be employed in compositions which have a tendency to produce excessive suds in use. Where a hydrocarbon solvent is present at a sufficiently high level this may itself provide some or all of the required antifoaming activity.

For example, the composition according to the invention may also comprise ingredients such as colorants, whiteners, optical brighteners, soil suspending agents, detersive
enzymes, compatible bleaching agents (particularly peroxide compounds and active chlorine releasing compounds), solvents, co-solvents, gel-control agents, further freeze-thaw stabilisers, bactericides, preservatives (for example 1^-benziso-'thiazolin-S-one), hydrotropes, polymers and perfumes.

Examples of optional enzymes include lipase, cellulase, protease, mannanase, amylase and pectate lyase.

**Viscosity of the liquid hard surface cleaning composition**

The liquid cleaning composition according to the invention preferably has a viscosity from 100 to 10,000 mPa.s, more preferably from 200 to 8,000 mPa.s, even more preferably from 400 to 6,500 mPa.s, and still even more preferably from 800 to 5,000 mPa.s, as measured at a shear rate of 20 s^{-1} and at a temperature of 25 degrees Celsius.

The viscosity can be suitable determined with a HAAKE viscotester VT550 (Gebruder HAAKE GmbH, Karlsruhe, Germany), using a 18/8 stainless steel MV measuring cup and a MV2 bob. Viscosity was measured at a shear rate of 20 s^{-1} and at a temperature of 25 degrees Celsius.

It will be appreciated that the viscosity of the composition according to the invention may be modified by adding a suitable viscosity enhancing or lowering agent as know in the art.

**Product Form**

The liquid hard surface cleaning composition according to the invention can be concentrated liquid, which may be diluted with for example water before use or may be read-to-use liquids. Preferably, the liquid compositions are pourable liquids.

**Packaging**

The compositions may be packaged in any form of container. Typically a plastic bottle with a detachable closure/pouring spout. The bottle may be rigid or deformable. A deformable bottle allows the bottle to be squeezed to aid dispensing. If clear bottles are used they may be formed from PET. Polyethylene or clarified polypropylene may be used. Preferably the container is clear enough that the liquid, with any visual cues
therein, is visible from the outside. The bottle may be provided with one or more labels, or with a shrink wrap sleeve which is desirably at least partially transparent, for example 50% of the area of the sleeve is transparent. The adhesive used for any transparent label should preferably not adversely affect the transparency.

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**Liquid Dispensers**

The liquid cleaning composition according to the invention may be stored and dispensed by any suitable means, but containers which allow easy and efficient application are preferred, such as pump or spray.

10

Preferably the composition according to the invention is packaged in a container comprising a spray dispenser. The spray dispenser may have any suitable mechanical means for ejecting the liquid in a spray or aerosol form, but more preferably is a (hand-driven) trigger spray.

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**Manufacturing process**

The liquid cleaning composition according to the invention may be manufactured by mixing the ingredients in any order. However, it will be appreciated that care should be taken as not to expose the calcite particles to acidic conditions for a prolonged amount of time. For example caustic soda may be used to regulate the pH of the liquid before adding the calcite particles. Preferably the polyethylenimine is added last.

20

**Method of cleaning**

Cleaning may be carried out by simply leaving the hard surface cleaning composition according to the invention in contact with the surface to be cleaned for a sufficient period of time. It will be appreciated that the composition is preferably applied to the hard surface area comprising the stains/soils. Particularly efficient cleaning was achieved when the applied liquid cleaning composition according to the invention is agitated on the hard surface by suitable means, such as by use of a brush or by rubbing. The agitation may essentially be carried out using any suitable mechanical devices known in the art. Preferably the visible liquid composition is removed from the hard surface (comprising stains/soils) by rinsing and/or by any other suitable gentle means such as by use of a cloth (e.g. microfiber cloth or squeegee).
Therefore the invention further relates to a method for the cleaning of a hard surface comprising the following steps:

a) application of the liquid composition according to the invention to the hard surface;

b) agitation of the applied composition on the hard surface;

c) optionally gently removing the visible liquid composition by rinsing, by use of a cloth or both.

It will be appreciated that the removal of the visible liquid composition from the hard surface at step 'c' of the cleaning method should be gentle in the sense that it allows at least some molecules of polyethylenimine to remain of the hard surface, which is believed important to provide a next-time cleaning benefit.

To maintain the next-time cleaning benefit, preferably the liquid cleaning composition according to the invention is applied to the hard surface on a regular basis. Preferably, said method is applied on average to a hard surface at least once every a 100 days, more preferably at least once every 50 days, even more preferably at least once every 25 days, still even more preferably at least once every 15 days and still even more preferably at least once every 7 days.

The invention will now be further described with reference to the following non-limiting examples.

EXAMPLES

Assessment of cleaning performance

A next-time cleaning performance was assessed using toughened dehydrated castor oil (DHCO, John L Seaton & Co, Humberside, UK) as stain/soil material and 10 x 10 cm tiles of brushed stainless steel as hard surface according to the following protocol:

First the surface of the steel tiles was prepared by soaking for about 1 hour in 50/50 w/w aqueous ethanol comprising 17 wt. % of potassium hydroxide. After soaking, the steel tiles were thoroughly rinsed with demineralised water, air-dried and stored vertically. After
drying, each steel tile was weighed to determine weight 'a' and a 5.0 x 5.0 cm square in the surface centre of each tile was marked by adhesive tape.

Next about 0.022 g of the cleaning liquid to be tested was mixed 1:1 with water and uniformly applied to the square surface area using a glass spreader. The cleaning liquid thus applied was left to dry at room temperature. Next the tile was rinsed with water for 2 seconds with a shower head at a flow rate of 6L/minute. The tiles were, air-dried and stored vertically.

About 0.040 g of DHCO was applied to the square area using a spreader, to produce an even film of oil after which the masking tape template was carefully removed. To simulate the oxidative toughening the tiles were heated in an oven at 100 degrees Celsius for 60 minutes. Subsequently, the tiles were allowed to cool for at least 1 hour. The tiles were reweighed (weight 'b') and the weight of the aged soil \( W_{\text{initial}} \) calculated by subtracting the weight 'a' from weight 'b'.

The tile surface to which the soil was applied was cleaned using a Martindale Abrasion Tester apparatus (SDL International). Each soiled tile was fixed in an abrasion tester's sample well and 20g of detergent base was introduced (5.0% Neodol 91-8 in water with a pH of about 6). The Tester was fitted with cleaning heads weighing 994 gram and applying about 660 gram/cm² of force to the tile surface. The cleaning heads were provided with a 1.5 cm diameter circle of non-woven cleaning cloth ('Ballerina', J. Dittrich & Sohne Vliesstoffwerk GmbH)). Cleaning was carried out for one full lissajous (16 cycles). During a full lissajous the entire soiled (square) surface is treated.

After treatment in the Martindale, the tiles were removed, rinsed with water, air-dried and weighed to determine weight 'c'. The weight of any remaining DHCO soil \( W_{\text{final}} \) was calculated by subtracting weight 'a' from weight 'c'.

Cleaning performance is calculated from the \( W_{\text{initial}} \) and \( W_{\text{final}} \) and expressed as wt. % soil removal:
Soil Removal (%) = \( \frac{W_{\text{initial}} - W_{\text{final}}}{W_{\text{initial}}} \times 100\% \)

Preparation of cleaning compositions

The liquid cleaning compositions of Example 1, 2, 3 and 4 and Comparative A were prepared with a composition as set out in Table 1.

**Table 1. Composition of liquid cleaning compositions**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Wt. %</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
<th>Comp. A</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS Acid ¹</td>
<td>5.1</td>
<td>5.1</td>
<td>5.1</td>
<td>5.1</td>
<td>5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>Caustic soda</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>C16-C 18 fatty acid ²</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
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<tr>
<td>Acrylate copolymer ³</td>
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<tr>
<td>Silicone/silicate composite ⁴</td>
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<td>1,2-Benzisothiazolin-3-one ⁵</td>
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<td>0.016</td>
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<td>5</td>
<td>10</td>
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<td>calcite 65 AV ⁸</td>
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<td>10</td>
<td>5</td>
<td>10</td>
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<td>Polyethylenimine ⁹</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>-</td>
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<td>water</td>
<td>to balance</td>
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1. Linear alkylbenxene sulphonic acid.
2. Tradename: Priolene 6907; Supplier: Unichema
3. Tradename: Acusol 820; Supplier: Dow Chemicals
4. Tradename: Silicon DB 310; Supplier: Dow Corning
5. Tradename: Proxel GXL; Supplier: Avecia
6. Tradename: Lialet 125-5; Supplier: SASOL
7. Calcium carbonate particles, average particle about 35 micron; Supplier: Omya Greater South.
8. Calcium carbonate particles, average particle about 65 micron; Supplier: Omya Greater South.
9. Tradename Lupasol PS; Supplier: BASF

Preparation of the cleaning compositions.
Each of the liquid cleaning compositions of Example 1, 2, 3 and 4 and Comparative A were prepared in the following manner:

A first mixture was made by dissolving the LAS Acid and caustic soda were dissolved using about a third of the water. Subsequently the C16-C18 fatty acid and the acrylate copolymer were added to the first batch.

A second mixture was made by dissolving the silicone/silicate composite and 1,2-Benzisothiazolin-3-one in the remaining part of the water. Subsequently the sodium carbonate was mixed-in and thereafter the remainder of the ingredients, except for the polyethylenimine. For example, in case of Example 1, 2, 3 and 4, the remainder of ingredients comprised the calcite 30 AV and 65 AV in the amounts as indicated.

Next the first mixture and the second mixture were combined and mixture together. In case of Example 1, 2, 3 and 4, lastly the polyethylenimine was mixed-in as well.

Results
The effect was assessed according to the method described and the result shown in Table 2.
Table 2. Cleaning effect of the cleaning compositions

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<tr>
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<th>Soil removal (%)</th>
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<td></td>
<td>Average</td>
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<td>Example 1</td>
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<td>Example 2</td>
<td>40.8</td>
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<td>Example 3</td>
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<td>Example 4</td>
<td>61.0</td>
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<td>Comparative A</td>
<td>5.7</td>
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The results clearly show that the liquid cleaning compositions comprising both calcite particles and polyethylenimine (Examples 1, 2, 3 and 4) provide a superior next-time cleaning benefit compared to Comparative A comprising only calcite particles. Furthermore, clearly certain ratio's of calcite particles to polyethyleneimine provide superior (next-time) cleaning efficiency. The best cleaning results were obtained by the liquid cleaning composition of Example 3, comprising a calcite:polyethylenimine ratio of 50:1.
Claims

1. Liquid hard surface cleaning composition comprising
   - 10 to 95 wt. % of a liquid solvent; and
   - 0.1 to 75 wt. % of a surfactant; and
   - 5 to 60 wt. % of abrasive calcite particles; and
   - 0.01 to 10 wt. % of polyethylenimine;

   wherein the weight ratio of calcite particles to polyethylenimine is from 1:1 to 500:1 and
   wherein the pH of the liquid hard surface cleaning composition is at least 8.

2. Composition according to claim 1, wherein the polyethylenimine has an average
   molecular weight of 10,000 to 5,000 000; preferably from 50,000 to 2,000,000; more
   preferably from 100,000 to 1,500,000 and even more preferably from 500,000 to
   1,000,000 Dalton.

3. Composition according to claim 1 or claim 2, wherein the polyethylenimine has an
   average cationic charge density from 5 to 35 meq/g, more preferably from 10 to 30 meq/g
   and even more preferably from 15 to 25 meq/g and still even more preferably from 18 to
   22 meq/g.

4. Composition according to any one of claims 1 to 3, comprising polyethylenimine in an
   amount of from 0.02 to 5 wt. %, more preferably from 0.04 to 2 wt. %, even more
   preferably from 0.06 to 1 wt. % and still even more preferably from 0.08 to 0.5 wt. %.

5. Composition according to any one of claims 1 to 4, wherein the amount of calcite
   particles is from 6 to 50 wt. %, preferably from 7 to 40 wt. %, more preferably from 8 to 30
   wt. % even more preferably from 9 to 25 wt. %.

6. Composition according to any one of claims 1 to 5, wherein the mean volume average
   size of the calcite particles is from 0.1 to 500 μηη, more preferably from 1 to 250 μηη, even
   more preferably from 5 to 150 μηη, still even more preferably from 10 to 75 μηη and still
   even more preferably from 25 to 70 μηη.
7. Composition according to any one of claims 1 to 6, wherein the weight ratio of calcite particles to polyethylenimine is from 10:1 to 400:1, preferably from 20:1 to 300:1, more preferably from 30:1 to 200:1, even more preferably from 35:1 to 150:1, still even more preferably from 40:1 to 125:1 and still even more preferably from 45:1 to 75:1.

8. Composition according to any one of claims 1 to 7, wherein the amount of surfactant is from 1 to 50 wt. %, more preferably from 2 to 25 wt. % and even more preferably from 3 to 10 wt. %.

9. Composition according to any one of claims 1 to 8, wherein the claim 8, wherein the surfactant comprises at least 50 wt. %, more preferably 75 wt. % and still even more preferably at least 95 wt. % of anionic surfactant, based on the total amount of surfactant.

10. Composition according to any one of claims 1 to 9, wherein the composition comprises 35 to 92 wt. %, preferably 55 to 90 wt. % and more preferably 65 to 85 wt. % of liquid solvent.

11. Composition according to any one of claims 1 to 10, wherein the composition comprises at least 50 wt. %, preferably at least 75 wt. %, more preferably at least 85 wt. % and even more preferably at least 95 wt. % of water, based on the total weight of liquid solvent.

12. Composition according to any one of claims 1 to 11, wherein the composition has a pH of at least 8.5, more preferably at least 9, even more preferably at least 9.5, still even more preferably at least 10, still even more preferably at least 10.5 and still even more preferably at least 11.

13. Container comprising the liquid composition according to any one of claims 1 to 12, wherein the container is a spray dispenser and preferably a hand driven trigger spray dispenser.

14. A method for the cleaning of a hard surface comprising the following steps:
a) application of the liquid composition according to any one of claims 1 to 12, to the hard surface;
b) agitation of the applied composition on the hard surface;
c) optionally gently removing the visible liquid composition by rinsing, by use of a cloth or both.

15. A method according to claim 14, wherein the method is applied to a hard surface on average at least once every a 100 days, more preferably at least once every 50 days, even more preferably at least once every once every 25 days, still even more preferably at least once every 15 days and still even more preferably at least once every 7 days.
## INTERNATIONAL SEARCH REPORT

**International application No**

PCT/EP2013/074141

### A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/12  C11D3/37  C11D17/00

ADD.

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

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

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

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

EPO-Internal, WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>DE 10 2004 057623 AI (HENKEL KGAA [DE]) 1 June 2006 (2006-06-01) claims; examples</td>
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Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:
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  - "O" - document referring to an oral disclosure, use, exhibition or other means
  - "P" - document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search: 21 February 2014

Date of mailing of the international search report: 17/03/2014

Name and mailing address of the ISA:
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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax. (+31-70) 340-3016

Authorized officer: Pfannenstein, Heide

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