Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2472183 A1 2003/09/04

(21) 2 472 183

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2003/01/31
(87) Date publication PCT/PCT Publication Date: 2003/09/04
(85) Entrée phase nationale/National Entry: 2004/06/29
(86) N° demande PCT/PCT Application No.: EP 2003/000988
(87) N° publication PCT/PCT Publication No.: 2003/072689
(30) Priorité/Priority: 2002/02/28 (02251405.3) EP

(51) Cl.Int.^{7}/Int.Cl.^{7} C11D 3/39
(71) Demandeur/Applicant:
UNILEVER PLC, GB
(72) Inventeurs/Inventors:
ASHCROFT, ALEXANDER THOMAS, GB;
VAN DEN BERGH, CARLO JOHANNES, IT;
SCHIAVINA, ANNALISA, IT
(74) Agent: BERESKIN & PARR

(54) Titre : COMPOSITIONS DE NETTOYAGE LIQUIDES
(54) Title: LIQUID CLEANING COMPOSITIONS

(57) Abrégé/Abstract:

The invention provides a process for removing fatty soil from a hard surface, the process comprising the steps, in sequence, of: (a) treating the hard surface with a liquid cleaning composition comprising a radical scavenging antioxidant and hydrogen peroxide; (b) allowing the fatty soil to deposit; and (c) cleaning the surface to remove the fatty soil. Preferably natural antioxidants are used in the process. The invention also provides liquid hard surface cleaning compositions comprising a natural radical scavenging antioxidant, hydrogen peroxide and preferably a surfactant.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 September 2003 (04.09.2003)

PCT

(10) International Publication Number
WO 03/072689 A1

(51) International Patent Classification^7: **C11D 3/39**

(21) International Application Number: PCT/EP03/00988

(22) International Filing Date: 31 January 2003 (31.01.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02251405.3 28 February 2002 (28.02.2002) EP

(71) Applicant *(for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only)*: **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant *(for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only)*: **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London, Greater London EC4 4BQ (GB).

(71) Applicant *(for IN only)*: **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

(72) Inventors: ASHCROFT, Alexander, Thomas; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **VAN DEN BERGH, Carlo, Johannes**; Lever Fabergé Italia SRL, Via Lever Gibbs, I-26841 Casalpusterlengo (IT). **SCHIAVINA, Annalisa**; Lever Fabergé Italia SRL, Via Lever Gibbs 3, I-26841 Casalpusterlengo (IT).

(74) Agent: DEKKER, Enno, E., J.; Unilever NV, Patent Department, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/072689 A1

(54) Title: LIQUID CLEANING COMPOSITIONS

(57) Abstract: The invention provides a process for removing fatty soil from a hard surface, the process comprising the steps, in sequence, of: (a) treating the hard surface with a liquid cleaning composition comprising a radical scavenging antioxidant and hydrogen peroxide; (b) allowing the fatty soil to deposit; and (c) cleaning the surface to remove the fatty soil. Preferably natural antioxidants are used in the process. The invention also provides liquid hard surface cleaning compositions comprising a natural radical scavenging antioxidant, hydrogen peroxide and preferably a surfactant.

Liquid cleaning compositions

FIELD OF THE INVENTION

The present invention relates to liquid cleaning compositions comprising antioxidants and peroxides and to a process for cleaning hard surfaces using these compositions.

BACKGROUND TO THE INVENTION

Household surfaces are normally cleaned using compositions which contain one or more ingredients which assist removal of fatty/oily/greasy soil and/or any visible staining such as from associated solid debris or coloured material. Such compositions may be applied neat or in dilute solution, by pouring or as a spray, such as from a trigger spray dispenser or other aerosol applicator, and rubbed with a cloth or other wipe, optionally followed by rinsing.

JP-A-07/228,892 discloses hard surface cleansing compositions comprising anionic and amphoteric surfactants, a mono- or polyhydric alcohol and from 0.1% to 7% by weight of a tea leaf extract. Tannins are commonly known to be an ingredient of tea, but tannic acid (an antioxidant) is present only in very small quantities in such extracts. Tannins are said to generally adversely affect cleaning, especially of oily soil.

Other disclosures of using extracts of tea or other leaves in hard surface cleaning and/or disinfecting products are in JP-A-07/228,890 and '891, JP-A-08/104,893, JP-A-10/273,698, JP-A-11/100,596, JP-A-06/340,897, JP-A-63/196,693, JP-A-62/167,400, JP-A-59/-047,300 and US 4,220,676, although the products disclosed in the latter two contain no surfactant.

US 5,965,514 discloses mildly acidic hard surface cleaning compositions containing amine oxide surfactant, quaternary disinfectant and a nitrogen-containing chelating agent. Ascorbic acid is mentioned among a large number of possible acids to provide acidity, but not among the preferred ones. Tannic acid is mentioned as one of a large number of optional possible acids useful as surface tension reducing agents.

An antifogging agent for glass is described in JP-A-49/113,811. This comprises by weight, 3% dialkyl sulfosuccinate anionic surfactant, 4% higher secondary alkoxyethyl sulfate anionic surfactant, 1% tannic acid, 10% propylene glycol, 5% isopropyl alcohol and 77% water.

US 5,602,090 discloses cleaning compositions containing easily oxidisable terpenes such as limonene and hydrogen peroxide. The example formulations contain 0.02% butylated hydroxyanisole as an antioxidant.

EP 209228, WO 97/02331, EP 844302, EP 1069178 and disclose fabric bleaching compositions comprising a surfactant, a peroxide bleach such as hydrogen peroxide and various radical scavengers. Propyl gallate, butyl-hydroxy anisole and partially hindered substituted hydroxybenzenes have been mentioned. Ascorbic acid and ascorbyl esters have been mentioned as additional components. US 6,110,883 discloses similar compositions having a pH above 8.

In US 6,296,880 farmaceutical skin cleansing compositions are disclosed for treating various skin conditions. The compositions contain an acidic compound like tannic acid, preferably in an amount of at least 1%, a certain amount of hydrogen peroxide and an antimicrobial agent in an amount sufficient to reduce microorganisms on the skin. The compositions may further include antioxidants.

However, it is nowhere disclosed in the prior art that the treatment of a surface with an antioxidant would have any positive effect on the subsequent removal of oily soil thereafter deposited on that surface.

EP 447553 disclosed bleaching compositions for cleaning hard surfaces comprising hydrogen peroxide or a precursor thereof, a peracid precursor that produces peracid with the hydrogen peroxide and optionally a surfactant. The peracid precursor is an alkoxylated aliphatic or araliphatic carboxylic acid. The peracid is produced immediately prior to use of the composition by mixing the hydrogen peroxide (or precursor) with the peracid precursor at pH of 5-13. Thus the hydrogen peroxide and the peracid precursor must be stored separately. An antioxidant is optionally added to the peracid precursor to prevent premature oxidation.

While it is known that hydrogen peroxide can be used for bleaching of coloured soil and stains on hard surfaces, it has been surprisingly found that hydrogen peroxide also generally assists in the removal of soil (whether coloured or not) from hard surfaces.

It has also been surprisingly found that certain antioxidants when present on a hard surface prevent oily soil later deposited on that surface from adhering thereto and thus facilitate subsequent removal of the oily soil.

Even more surprisingly it has been found that when hydrogen peroxide and these antioxidants are present together in a one-liquid cleaning composition both activities are retained independently without the hydrogen peroxide interfering with the activity of the antioxidant and vice versa. Also, the compositions are stable on storage without loss of hydrogen peroxide or antioxidant activity during storage.

Furthermore, there is a preference among consumers for mild ingredients in cleaning compositions, and natural ingredients, more particularly natural antioxidants, are generally perceived as being mild.

Brief description of the invention

Thus, in one aspect the present invention provides a process for removing fatty soil from a hard surface, the process comprising the steps, in sequence, of:

(a) treating the hard surface with a liquid cleaning composition comprising a radical scavenging antioxidant and hydrogen peroxide;

(b) allowing the fatty soil to deposit; and

(c) cleaning the surface to remove the fatty soil.

A second aspect of the present invention provides liquid cleaning compositions comprising hydrogen peroxide and a natural radical scavenging antioxidant.

A third aspect of the invention provides the use of a radical scavenging antioxidant and hydrogen peroxide together for removing fatty soil from a hard surface.

Detailed description of the invention

Whilst not being bound by any particular theory or explanation, it is believed that the radical scavenging antioxidant exerts its effect by being retained on the surface in step (a), so that fatty soil subsequently deposited on the surface in step (b) does not toughen or polymerise, thereby allowing easier removal of the soil in step (c). Therefore, one embodiment of the first aspect of the invention comprises formation of a film comprising the antioxidant in step (a), e.g. by leaving a solution or liquid composition comprising the antioxidant and the hydrogen peroxide to dry on the surface. Step (c) is advantageously effected using a hard surface cleaning composition again comprising the antioxidant and the hydrogen peroxide so that soil is removed and new antioxidant is applied at the same time, thus effectively combining step (c) of the first process according to the first aspect of the invention with step (a) of a subsequent process according to this aspect of the invention. Step (c) is optionally followed by a rinsing step, usually with water.

Again, whilst not being bound by any theory or explanation it is believed that hydrogen peroxide generally assists in soil removal by decomposition of hydrogen peroxide on the hard surface thus generating minuscule oxygen bubbles which help loosening and lifting the soil from the surface.

The antioxidant in the liquid composition used in the process may be any synthetic or natural radical scavenging antioxidant as hereinbelow further described. Preferably the antioxidant is a natural antioxidant. The liquid compositions preferable comprise at least 0.05% by weight of antioxidant, more preferably 0.1% - 10% by weight, even more preferably at least 0.2%. Amounts of more than 2% or even 1% are generally not required and less than 1% or even at most 0.5 are generally sufficient. Mixtures of antioxidants may be used as well.

The compositions used in the process also comprise hydrogen peroxide, preferably in an amount of 0.1-10%, more preferably at least 1%. Higher amounts than 5% are generally not required and may cause damage to sensitive surfaces.
The compositions used in the process optionally, but preferably contain one or more surfactants as hereinbelow further described. Additionally they may contain other optional ingredients conventionally used in cleaning compositions.

As used herein, the term "soil" encompasses all kinds of staining or soiling of organic or inorganic origin, whether visible or invisible to the naked eye, including soiling of solid debris and/or with bacteria or other pathogens. As outlined, the invention is particularly effective for easier removal of fatty soil, more specifically aged or baked-on fatty soil. Usually such fatty soil, as often found e.g. on kitchen surfaces, comprises an oil/fat component in combination with other soil components such as food remains of starchy and/or proteinaceous nature, dust, lime scale deposits, etc. The invention is also effective for removing lime scale, water marks and similar stains.

The present invention may also deliver one or more other benefits such as improved tactile properties of the surface (e.g. smoothness) during and/or after cleaning, reduction of rancid smell and less darkening of the soil before cleaning, less surface corrosion and less noise during cleaning.

Methods, uses and compositions and other products according to the present invention are useful for treating any household hard surfaces in for example kitchens and bathrooms including cooker tops, extractor fans, work surfaces, cooking utensils, crockery, tiles, floors, baths, toilets, wash basins, showers, dishwashers, taps, sinks, and glass and enamel surfaces in general. These surfaces may, for example, consist of paint (e.g. painted or lacquered wood), plastics, glass, ceramic or metal (e.g. stainless steel or chrome).

Antioxidants

As disclosed in Ingold K.V. Adv.Chem.Ser.75, 296-305 (1968) "Inhibition of Auto-oxidation", antioxidants fall into two groups, namely primary or chain-breaking antioxidants which react with lipid radicals to form more stable radicals, and secondary (or preventative) antioxidants which reduce the rate of chain initiation by various mechanisms. Further antioxidants may be classified as synthetic or "natural", i.e. derived from natural products.

The following are classes, sub-classes and specific examples of antioxidants, which may be used in methods, uses, articles and compositions according to the present invention. As used herein, the term "antioxidant" in the singular embraces one antioxidant as well as two or more antioxidant materials in combination.

A. Synthetic Antioxidants

In general, primary antioxidants are subdivided into chain-breaking acceptors and chain-breaking donors.

Chain-breaking acceptors (sometimes called "preventative antioxidants") reduce oxidation rates by decomposing hydroperoxides into (non-radical) stable end products.

Chain-breaking donors, also called "hydrogen-donating antioxidants or radical scavengers, function by competing with organic materials for peroxy radicals.

B. Natural Antioxidants

Natural antioxidant compounds are particularly preferred. Natural components have a particular appeal to many consumers. Particularly preferred are those antioxidants that are considered to be safe for use on surfaces that may come into contact with food preparations.

Diverse sources of natural materials exhibiting antioxidant activity have been reported including herbs, spices, cereals, coffee and beans, oils and seeds, tea leaves and protein hydrolysates. The active compounds, isolated from the extracts, responsible for exhibiting antioxidant activity include compounds from the chemical classes: tocopherols, flavanoids, phospholipids, organic acids and their derivatives, tannins, melanoidins, terpenoids, sterols, Maillard reaction products and amino acids. Depending on the structure the antioxidants may be water-soluble or oil-soluble; both types are useful for the present invention.

Carnosol, carnosic acid, rosmanol, rosmarinic acid, rosmariquinone and rosmaridiphenol are known as active components of rosemary leaves which exhibit antioxidant activity. Furthermore, two major phenolic antioxidant components, gallic acid and eugenol are derived from cloves. Of the large number of compounds isolated from the extracts of herbs and spices such as sage, marjoram, oregano and thyme, some are known to have potent antioxidant properties. Other natural antioxidants include β-carotene, caffeic, quinic and ferulic acid, and esters of caffeic acid with sterols (sitosterol, campesterol, gramisterol and cycloartenol). The sterol and triterpene alcohol esters of caffeic acid are not suitable. Further such compounds known to exhibit potent antioxidant activity include cinnamic, sinapic, vanillic, syringic and coumaric acids.

Cardanol is a mixture of monohydroxyl phenols with a meta (3-) 15-carbon chain on the phenyl ring. It is isolated as a distillate from cashew nut shell liquid. Anacardic acid (3-n-pentadecylsalicylic acid) is the main component (80-85%) while cardanol (3-n-pentadecyl-phenol) and cardol (3-n-pentadecyl-resorcinol) and methyl cardanol (2-methyl-5-n-pentadecyl-resorcinol) are present in smaller amounts. Cardol and cardanol are commercially available. Oryzanol refers to a group of esterified sterols, which have been reacted with ferulic acid (4-hydroxy-3-methoxycinnamic acid) having high molecular weight and low volatility. Sesamol, sesaminol and sesamolino compounds are constituents of sesame oil and have antioxidant properties. Sesamol readily undergoes oxidation to sesamol dimer and further oxidation yields the sesamol quinone dimer.

Tocopherols provide strong antioxidant activity. Under certain conditions tocopherols can form higher molecular weight materials in oils e.g. dimers, trimers, etc. Tocotrienols are a related class of compounds with the structural difference being an unsaturated side chain instead of a saturated phytyl chain. The antioxidant activity of tocotrienols is less than that exhibited by tocopherols.

The class of flavanoids is divided into subgroups of which the major members include flavanols, flavones, isoflavones, anthocyanins, catechins, proanthocyanidins and aurones. Related compounds include cinnamic and ferulic acids and their esters, some of which are precursors to flavanoids. Tealeaves are a rich, inexpensive and readily available source of flavanoids (mainly catechins). When oxidised the flavanoids form polymers with complex polyphenolic structures, themselves showing antioxidant activity. Epigallocatechin gallate can be extracted from tea in synergism with ascorbic acid, tocopherol, citric and tartaric acids.

Rutin and chlorogenic acid also exhibit antioxidant properties, having sugar moieties attached to aromatic functionality. Compounds of this type are particularly interesting since they can partition between aqueous and organic (lipid) phases.

Another group of natural antioxidants is the tannins, tannic acid and related compounds. It is a broad group of plant derived polyphenolic compounds. The tannins are characterised by their ability to precipitate proteins.

Antioxidant structure

Preferred antioxidants for the purpose of this invention are natural antioxidants which contain a 1,2-dihydroxybenzene or 1,4-dihydroxybenzene substructure, or a derivative thereof in which the H of one OH has been replaced by an organic group. The organic group may be -R or -COR wherein R is preferably a (substituted) alkyl, alkenyl, carbocyclic or heterocyclic group

Suitable examples of compounds having the 1,2-dihydroxybenzene(derivative) substructure are caffeic, ferulic, rosmarinic, and vanillic acid and their amides, esters, salts and similar derivatives, as well as sesamol and its derivatives. Suitable examples of compounds having the 1,4-dihydroxybenzene derivative substructure are the tocopherols and tocotrienols wherein part of the benzene ring and one of the phenolic oxygens together form part of a condensed heterocyclic ring.

A specific and very useful subclass of compounds having the 1,2-dihydroxybenzene substructure is formed by those having the 3,4,5-trihydroxybenzoyl structure or substituted derivatives thereof. Thus, gallic acid and its natural derivatives are suitable. Particularly suitable are tannic acid and tannins. Tannic acid and tannins contain a plurality of 3,4,5-trihydroxybenzoyl units whereby the benzoyl group of one unit forms an ester bond with a phenolic oxygen of the next unit.

Tannic acid is the most preferred antioxidant for the purposes of this invention. It is sometimes denoted as gallotannic acid or penta-(m-digalloyl)-glucose ($C_{76}H_{52}O_{46}$). However, commercially available tannic acid is usually obtained from plant or nut galls, tree barks and other plant parts. The term "tannic acid" as used herein is to be taken to embrace all such materials. As already mentioned, tannin-containing extracts of tea (e.g. as utilised in the compositions of JP-A-07/228,892) are very low in tannic acid content.

Another preferred group of antioxidants are the tocopherols, particularly δ-tocopherol.

The liquid compositions

The compositions may be applied to the surface neat or in diluted form. Suitable liquid compositions include solutions, dispersions or emulsions of the antioxidant material in a solvent. The solvent is preferably water, or a mixture of organic solvent and water.

Preferred compositions have a neutral or slightly acidic pH i.e. at most 7, preferably at most 6, especially at most 5.5 or even 4.5 or less. However, it is preferred that the compositions should not be too acidic, in order to avoid damage to acid sensitive surfaces; preferably the pH is at least 1.5 or even 2, more preferably at least 2.5. Most preferably, the pH is in the region from 3 to 4.5.

The liquid composition may be in the form of a thin or viscous liquid or gel or in the form of foam, mousse of paste. It is especially preferred if the liquid is viscous or gel-like having a viscosity of at least 100 mPas, preferably at least 150 or even 200 mPas, as measured at a shear rate of $21s^{-1}$ (Brookefield viscometer, 20°C), but preferably no more than 5,000 mPas, more preferably at most 2000 mPas. Shear thinning viscous liquids or gels enhance the pleasing sensory effect of the antioxidant during cleaning of a hard surface and are particularly appealing to the consumer and therefore a preferred embodiment of the invention. The viscosity may be brought about by an "internal structuring system" employing one or more surfactants, water, and (usually) electrolyte, to create an ordered or liquid crystalline phase within the composition. Alternatively or additionally a thickening polymer may be added, many of which are known in the art, for example polycarboxylate type polymers such as poly(meth)acrylates, polymaleic acids and copolymers of (meth)acrylic acid and/or maleic anhydride with various other vinylic monomers, or polysaccharides such as cellulose derivatives or vegetable or microbial gums e.g. xanthan gum, guar gum and the like. Of course the thickening polymers should be stable in the presence of hydrogen peroxide.

Foams and mousses are normally supplied from a dispenser who gassifies or aerates the product dispensed therefrom.

Preferred compositions are either low foaming, or if foaming or applied as a foam, the foam easily collapses, thus obviating the need to subsequently rinse or wipe the surface again to remove foam. Thereby the amount of antioxidant remaining on the surface is maximised.

Surfactants:

A composition according to (or for use in) the invention can comprise detergent surfactants which are generally chosen from anionic, nonionic, amphoteric, zwitterionic or cationic surfactants. The compositions generally comprise at least 0.05%, preferably at least 0.1, 0.2, 0.5 or even 1% by weight, but not more than 45% usually at most 25, 15 or even 10% by weight of total surfactant. Preferably the compositions comprise at least an anionic and/or nonionic surfactant, more preferably at least a nonionic surfactant.

Suitable synthetic (non-soap) anionic surfactants are water-soluble salts of organic sulphuric acid esters and sulphonic acids that have in the molecular structure an alkyl group containing from 8 to 22 carbon atoms.

Examples of such anionic surfactants are water soluble salts of:

- (primary) long chain (e.g. 8-22 C-atom) 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;

- alkyl benzene sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;

- secondary alkanesulphonates;

Also suitable are salts of:

- alkyl glyceryl ether sulphates, especially those ethers of the fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;
- sulphates of the reaction product of one mole of a fatty alcohol and from 1 to 6 moles of ethylene oxide;
- salts of alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
- the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali;

and mixtures of the above.

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 alkylbenzenesulphonates and mixtures with olefinsulphonates and alkyl 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 alkyl 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 compositions of the invention, it will generally be at least 0.2%, preferably at least 0.5%, more preferably at least 1.0%, but not more than 20%, preferably at most 10%, more preferably at most 8%.

Suitable nonionic surfactants can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is attached to any particular hydrophobic group can be readily adjusted to yield a water-soluble 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 product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the reaction product of ethylenediamine 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 examples are: alkylglycosides which are condensation products of long chain aliphatic alcohols and saccharides; tertiary amine oxides of structure RRRNO, where one R is an alkyl group of 8 to 18 carbon atoms and the other Rs are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure RRRPO, where one R is an alkyl group of 8 to 18 carbon atoms and the other Rs are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide; and dialkyl sulphoxides of structure RRSO where one R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans. Ethoxylated aliphatic alcohols are particularly preferred.

The amount of nonionic surfactant to be employed in the cleaning composition of the invention will preferably be at least 0.1%, more preferably at least 0.2%, most preferably at least 0.5 or even 1% by weight. The maximum amount is suitably 15%, preferably 10% and most preferably 7%.

The compositions may contain amounts of both anionic and nonionic surfactants which are chosen, bearing in mind the level of electrolyte present, so as to provide a structured liquid detergent composition, i.e. one which is 'self-thickened'. Thus, in spite of the presence of organic solvent, thickened liquid cleaning compositions can be made without the need to employ any additional thickening agent and which nevertheless have a long shelf life over a wide temperature range.

The weight ratio of anionic surfactant to nonionic surfactant may vary, taking the above considerations in mind, and will depend on their nature, but is preferably in the range of from 1:9 to 9:1, more preferably from 1:4 to 4:1, According to an embodiment illustrating any aspect of the invention, the compositions may comprise from 0.1.% to 2% by weight of antioxidant(s), from 1 to 4% by weight of hydrogen peroxide, from 0 to 20%, preferably from 0.2% to 10% by weight of a water-soluble, synthetic anionic sulphate or sulphonate surfactant salt containing an alkyl radical having from 8 to 22 carbon atoms in the molecule, and from 0.2 to 7% by weight of an ethoxylated nonionic surfactant derived from the condensation of an aliphatic alcohol having from 8 to 22 carbon atoms in the molecule with ethylene oxide, such that the condensate has from 2 to 15 moles of ethylene oxide per mole of aliphatic alcohol, the balance being other optional ingredients and water.

Suitable amphoteric surfactants that optionally can be employed are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 18 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 N-2-hydroxydodecyl-N-methyl taurate.

Suitable cationic surfactants that optionally can be employed are quaternary ammonium salts having one or two aliphatic groups of from 8 to 18 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethyl ammonium bromide.

Suitable zwitterionic surfactants that optionally can be employed are 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 3-(N,N-dimethyl-N-hexadecylammonium) propane-1-sulphonate betaine, 3-(dodecyl methyl sulphonium) propane-1-sulphonate betaine and 3-(cetylmethyl phosphonium) ethane sulphonate betaine.

Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents" Vol.1, by Schwartz & Perry, Interscience 1949, Vol.2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of

"McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

The compositions according to the invention can contain other ingredients which aid in their cleaning performance. For example, the composition can contain detergent builders such as nitrilotriacetates, polycarboxylates, citrates, dicarboxylic acids, water-soluble phosphates (especially ortho-, pyro- or poly-phosphates or mixtures thereof), zeolites and mixtures thereof in an amount of up to 25%. If present, the builder preferably will form at least 0.1% of the composition.

Metal ion sequestrants such as ethylenediaminetetraacetates, polyphosphonates (DEQUEST[TM]-range) and the (ortho, pyro, poly) phosphoric acids/phosphates (hereinafter collectively referred to as "phosphate"), and a wide variety of poly-functional organic acids (particularly citric acid) and salts, can also optionally be employed provided they are compatible with the antioxidant. Such sequestrants are particularly useful when combined with antioxidants which may form coloured complexes with metals, such as is the case for tannic acid, tannins and gallic acid and derivatives. The amount of such sequestrants, if present, is usefully between 0.05 and 5% by weight of the composition, preferably 0.1-1%.

A further optional ingredient for compositions according to the invention is a suds regulating material, which can be employed in compositions which have a tendency to produce excessive suds in use.

One example of a suds regulating material is soap. Soaps are salts of fatty acids and include alkali metal soaps such as the sodium, potassium and ammonium salts of fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 10 to about 20 carbon atoms. Particularly useful are the sodium and potassium and mono-, di- and triethanolamine salts of the mixtures of fatty acids derived from coconut oil and ground nut oil. When employed, the amount of soap can form at least 0.005%, preferably at least 0.1% by weight of the composition. Fatty acid soaps such as Prifac 7901[TM] have been found to be suitable for this purpose.

A further example of a suds regulating material is a silicone oil. Where a hydrocarbon co-solvent is present at a sufficiently high level this may itself provide some or all of the desired antifoaming activity.

Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as colorants, whiteners, optical brighteners, soil suspending agents, detersive enzymes, gel-control agents, freeze-thaw stabilisers, preservatives (for example 1,2-benzisothiazolin-3-one), and hydrotropes. However, compositions according to the invention do not contain bactericides (other than hydrogen peroxide) in amounts suitable to provide an antibacterial action on the skin. Generally, bactericides, if present, are only used in amounts necessary to prevent microbial spoilage of the composition.

As the compositions according to the invention and their use for cleaning hard surfaces depend on the presence of hydrogen peroxide, they do not contain alkoxylated aliphatic or araliphatic carboxylic acids as precursors for the corresponding peracids.

Dispensing

Liquid compositions may be stored and dispensed by any suitable means, such as by spray applicators. Pump dispensers (whether spray or non-spray pumps) and pouring applicators (bottles etc) are also possible. The compositions may also applied to the surface with a wipe impregnated with the liquid composition.

EXAMPLES

In the following examples, all percentages are by weight unless specifically stated otherwise.

Example 1: General purpose cleaning composition

Biodac L6S50 (nonionic)	1.2%
LAS (anionic)	3.5%
Tannic acid	0.50%
Hydrogen peroxide	3.0%
Phosphoric acid	0.42%
Sodium hydroxide	0.046%
Urea	1,0%
Perfume	0.35%
Dequest 2046	0.10%
Coconut fatty acid (Prifac 7907™)	0.30%
Water	to 100%

Control 1

As Example 1 but without tannic acid.

Evaluation

Substrate Details

A stainless steel substrate was used for cleaning tests. This was brushed stainless steel size 380mm by 300mm (grade 304 sheet BS 1449 Pt2 1983, supplied by Merseyside Metal Services Ltd). This size tile accommodates two areas for cleaning, one on the left and one on the right of the tile. Each area for cleaning is 215mm by 150mm.

Pre-cleaning of Stainless Tiles

The tiles were pre-cleaned prior to a cleaning experiment as follows:

- commercial liquid abrasive cleaner (Jif Cream cleaner), cleaning with a damp J-cloth and rinsed with hot water;
- liquid dish-washing detergent (Persil Dishwashing Liquid), cleaning with a damp J-cloth and rinsed with hot water;
- calcite, cleaning with a damp J-cloth and rinsed hot water, and finally rinsed with demineralised water;
- after allowing the tiles to drain-dry, they are wiped with a paper towel, ensuring all calcite deposits are removed.

Application of Pre-treatment to Stainless Steel Tiles

A cardboard mount revealing the two areas of the tile to be pre-treated was placed onto the stainless steel tile. To one of the 215mm x 150mm areas, approximately half of a 1.0ml pipetted aliquot of an example composition was applied in a line across the top 150mm section of the pre-treatment area. The remaining portion of the 1.0ml example composition was similarly applied to the lower 150mm section of the area. The cardboard mount was carefully removed from the steel tile in readiness to wipe the applied prototype over the entire pre-treatment area. A dampened hand-wrung J-cloth™ (demineralised water) was folded around a 150mm plastic ruler. This was used to spread the 1.0ml aliquot of the composition being tested, over the steel surface. The prototype was spread using four linear wipes over the designated area, two downward and two upward wipes, and in each case 4 replicates for cleaning were prepared. After pre-treatment application, the tiles were allowed to dry for 2 hours before spraying with dehydrated castor oil soil.

Soiling and Ageing the Pre-treated Stainless Steel Tiles

The spraying of the castor oil soil was carried out in a fume cupboard under standard conditions to ensure good reproducibility between different experiments. The soil was dehydrated castor oil with 0.2% fat red 7B dye. This was stored in the refrigerator when not in use. It was equilibrated to ambient temperature before spraying.

The fume cupboard walls/floor and the lab-jack were covered with paper towel. A lab-jack was used to elevate the tile to a practical height for spraying. The lab-jack height was 200mm and was positioned centrally at the back of the fume cupboard. A line 40mm from the back wall of the fume cupboard was marked on to the top of the lab-jack, this was used as the positioning line for each steel tile before spraying. From the 40mm line on the lab-jack, a line 270mm, in parallel, was marked on the base of the fume cupboard floor. This was where the Perspex spray guide was aligned when spraying.

A commercially available gravity fill spray gun was used to spray the oily soil onto the steel tile. The rear dial on the gravity fill gun was rotated 360° anti-clockwise from the closed position and the side dial was rotated 270° anti-clockwise, again from the closed position. The gravity fill spray gun was attached to a floor standing air compressor unit and a pressure of 25p.s.i. was used for spraying this soil on to the steel tiles. A clamp stand was positioned in the fume cupboard to hold the spray gun when not in use. The dehydrated castor oil soil was poured into the open bowl of the spray gun.

The cardboard spray mount was clipped to a stainless steel tile and this was centrally placed, in landscape position, on the lab-jack along the 40mm line from the rear of the fume cupboard. The cardboard spray mount was a rectangular piece of card, the same size as a stainless steel tile, with two cut-out areas sized 215mm by 150mm, one window area on the left side and the other to the right, with a card separator border between the two windows. The Perspex spray guide was positioned in front of the first window of the tile to be sprayed directly on the 270mm line. This area of the tile was sprayed for a total of 35 seconds starting from the top, following the line of the spray guide. The time taken to spray from top to bottom was approximately 9 seconds, therefore the track of the spray guide is traced 4 times, for each 215mm by 150mm area being sprayed. After spraying the first area of the tile, the adjacent area was sprayed in exactly the same way, after re-aligning the Perspex spray guide in front of the second area. Once the entire tile had been sprayed twice, it was removed from the fume cupboard and the cardboard spray mount carefully removed. The sprayed tiles were stacked directly on to an oven shelf, each stainless steel tile being separated using an aluminium ring spacer placed in each corner. These spacers enabled each tile to be separated by 10mm. When all the tiles were sprayed, they were collectively placed in the oven for ageing.

The tiles were aged at a temperature of 85°C for 1.5 hours. The prepared tiles were not cleaned until the next day.

The effort used to remove the soil from the test surface using a cellulosic spongecloth was measured on equipment specifically build for the purpose which measures the effort in Ns. The cleaning composition used to remove the soil was the composition of Control 2. Thus, the reduction in cleaning effort can only be attributed to the antioxidant in the pre-treatment composition

The results for the compositions of Example 1 and the control 1 (corresponding to Example 1 minus the tannic acid) are given in Table I. Results given are geometric means of the 4 replicate experiments.

Table I

Treatment	Average Total Effort (Ns)
No treatment (not clean in 2 minutes)	8000
Control 1	4500
Example 1	30

CLAIMS

1. A process for removing fatty soil from a hard surface, the process comprising in sequence the steps of:

   (a) treating the hard surface with a liquid cleaning composition comprising 0.1-10% by weight of hydrogen peroxide and 0.05%-10% by weight of a natural radical scavenging antioxidant comprising a 1,2-dihydroxybenzene or 1,4-dihydroxybenzene substructure;

   (b) allowing the fatty soil to deposit; and

   (c) cleaning the surface to remove the fatty soil.

2. A process according to claim 1 wherein also in step (c) a liquid cleaning composition is used comprising said radical scavenging antioxidant and hydrogen peroxide.

3. A process according claims 1 or 2 wherein the radical scavenging antioxidant has a 1,2-dihydroxybenzene substructure.

4. A process according to claim 3 wherein the radical scavenging antioxidant has the 3,4,5-trihydroxybenzoyl substructure.

5. A process according to claim 4 wherein the radical scavenging antioxidant is tannic acid.

6. A process according claims 1 or 2 wherein the radical scavenging antioxidant has a 1,4-dihydroxybenzene substructure.

7. A process according to claim 6 wherein the radical scavenging antioxidant is δ-tocopherol

8. A process according to claims 1-7 wherein the liquid cleaning composition has pH 7 or below.

9. A process according to claims 1-8 wherein the the liquid cleaning composition comprises 0.1%-1% by weight of the antioxidant.

10. A process according to claims 1-9 wherein the cleaning composition comprises a surfactant.

11. A process according to claims 1-10 wherein the surface is not rinsed after step a

13. Liquid storage-stable cleaning composition comprising 0.1-10% by weight of hydrogen peroxide and 0.05-10% by weight of a natural radical scavenging antioxidant comprising a 1,2-dihydroxybenzene or 1,4-dihydroxybenzene substructure, with the proviso that the compositions does not contain bactericides (other than hydrogen peroxide) in an amount suitable to provide an antibacterial action on the skin.

13. Liquid cleaning composition according to claim 12 additionally comprising 0.05-45% by weight of a surfactant.

14. Liquid cleaning composition according to claims 12-13 wherein the amount of the antioxidant is 0.1%-1.0% by weight

15. Liquid cleaning composition according to claims 12-14 wherein the radical scavenging antioxidant has a 1,2-dihydroxybenzene substructure.

16. Liquid cleaning composition according to claim 15 wherein the radical scavenging antioxidant has a 3,4,5-trihydroxybenzoyl substructure.

17. Liquid cleaning composition according to claim 16 wherein the radical scavenging antioxidant is tannic acid.

18. Liquid cleaning composition according to claims 12-14 wherein the radical scavenging antioxidant has a 1,4-dihydroxybenzene substructure.

19. Liquid cleaning composition according to claim 18 wherein the radical scavenging antioxidant is δ-tocopherol

20. Liquid cleaning composition according to claims 12-19 wherein the pH is 7 or below.

21. Use of a natural radical scavenging antioxidant and hydrogen peroxide in a liquid cleaning composition for facilitating the removal from a hard surface of fatty soil which has deposited on the surface after the treatment with the liquid cleaning composition.

22. Use according to claim 21 wherein in the cleaning composition the antioxidant is present in an amount of 0.05-10% by weight and the hydrogen peroxide in an amount of 0.1-10% by weight.

23. Use according to claims 21-22 wherein the antioxidant has a 1,2-dihydroxybenzene substructure.

24. Use according to claim 23 wherein the antioxidant has a 3,4,5-trihydroxybenzoyl substructure.

25. Use according to claim 24 wherein the antioxidant is tannic acid.

26. Use according to claims 21-22 wherein the antioxidant has a 1,4-dihydroxybenzene substructure.

27. Use according to claim 26 wherein the antioxidant is δ-tocopherol.

28. Use according to claims 21-27 wherein the liquid cleaning composition has pH 7 or below.