

(19) AUSTRALIAN PATENT OFFICE

(54) Title
Composition for cleaning hard surfaces

(51) ⁶ International Patent Classification(s)
C11D 17/00 060408BMEP
(2006.01) C11D 3/14
C11D 3/14 20060101ALI20
(2006.01) 060408BMEP
C11D 17/00 PCT/EP01/1188
20060101AFI20 1

(21) Application No: 2002220627 (22) Application Date: 2001.10.15

(87) WIPO No: W002/38720

(30) Priority Data

(31) Number	(32) Date	(33) Country
00203831	2000.11.03	EP

(43) Publication Date : 2002.05.21
(43) Publication Journal Date : 2002.07.25

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(56) Related Art
WO 2000/036078
WO 1997/041204
US 5741770

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
16 May 2002 (16.05.2002)

PCT

(10) International Publication Number
WO 02/38720 A1

(51) International Patent Classification: **C11D 17/00**,
3/14, 3/12

(21) International Application Number: PCT/EP01/11881

(22) International Filing Date: 15 October 2001 (15.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00203831.3 3 November 2000 (03.11.2000) EP

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(81) Designated States (national): AE, AG, AI, 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, GR, GU, 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, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

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

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- entirely in electronic form (except for this front page) and available upon request from the International Bureau

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 02/38720 A1

(54) Title: COMPOSITION FOR CLEANING HARD SURFACES

(57) Abstract: The invention provides liquid abrasive cleaning compositions for hard surfaces which are clear aqueous liquid gels comprising one or more detergent surfactants and macroscopic abrasive particles which are dispersed through the liquid. The gel and the particles preferably have different colours. The particles preferably have fairly uniform particle diameters of between 0.3 and 2.5mm. The invention also provides a process for cleaning hard surfaces comprising the step of applying a composition according to the invention to the surface.

Composition for cleaning hard surfaces

5 Field of the invention

The present invention relates to liquid compositions for cleaning hard surfaces. Particularly, the invention relates to clear liquid cleaning gels containing macroscopic solid
10 particles.

Background to the invention

15 Liquid abrasive cleaning compositions for hard surfaces are well known in the art. They generally have a milky white appearance. They have sufficient viscosity at low shear stress to keep the fine abrasive particles evenly dispersed in the liquid, while at the same time they behave as true
20 liquids when being dispensed from a bottle. The fine abrasive particles (powder) in these compositions generally have a particle size below 200 micron, in most cases below 100 micron. Well known abrasives used in such compositions are silica, calcite, feldspar and similar inorganic
25 materials as well as several organic polymer particles, all with a Moh hardness of up to 6. Although many consumers extensively use such compositions, some do not appreciate the feel or appearance of these products, or fear that they might scratch their delicate surfaces.

30

Some liquid abrasive products on the market consist of a gel-like opaque liquid in which a variety of coarse and

fine irregularly shaped abrasive polymer particles are dispersed varying in diameter between more than 1 mm at one end and hardly visible to the naked eye at the other end. Because of this the total product appearance is
5 unattractive. Thus, there is a need for a new liquid hard surface cleaning product containing solid particles, which is visually appealing to the consumer and at the same time cleans effectively.

10 In the skin cleansing art products exist which are known as facial scrubs and which consist of a clear viscous liquid in which coarse abrasive particles are dispersed. Since such products are in intensive contact with the skin, they must have about neutral pH. They generally contain little
15 or no detergent surfactant and to the extent that they do, such surfactants are chosen from those which are skin-friendly and generally expensive. Such products are developed specifically for cleaning skin and are generally unsuitable for any other purpose, more specifically for
20 removing tough soil from hard surfaces.

In US 5,741,770 and in WO97/41204 liquid crystal cleaning compositions are disclosed which are transparent or slightly turbid and contain small amounts of abrasive
25 particles. The particles may be zeolites with a mean particle size of 8-10µm, amorphous silica with a particle size of up to 300µm or polyethylene powder with a particle size of up to 500µm

30 WO00/65019 discloses liquid abrasive cleaning compositions containing a fine particulate abrasive and in addition thereto microcapsules containing various additional

components such as perfume, silicone oil and the like. In view of the specified amount and particle size of the abrasive, the compositions are clearly not transparent or translucent.

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WO00/36078 discloses pourable transparent laundry detergent compositions, containing at least 15% surfactant. The compositions are thickened to be able to suspend macroscopic capsules containing ingredients that are
10 desirably kept separate from the concentrated and highly alkaline detergent solution. Similar compositions, also for other applications, are disclosed in GB 1303810. The capsules do not have abrasive properties.

15 Thus, although various liquid compositions containing suspended particles in a large variation of particle size and undisclosed shape are described in the prior art for various purposes and applications, methods and measures to increase the visual appearance of such compositions to the
20 consumer appear to have been neglected.

Brief description of the invention

25 The invention provides liquid cleaning compositions for hard surfaces which are clear aqueous liquid gels comprising one or more detergent surfactants and macroscopic abrasive particles, which are dispersed in a stable fashion through the liquid.

30

The invention further provides a process for cleaning hard surfaces comprising the step of applying to the surface a

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clear aqueous liquid gel which comprises one or more detergent surfactants and macroscopic abrasive particles which are evenly dispersed through the liquid.

- As now claimed, according to one aspect of the present invention there is provided a clear aqueous gel liquid abrasive hard surface cleaning composition comprising one or more detergent surfactants and 0.1 to 20 wt% abrasive particles characterised in that the abrasive particles dispersed in the liquid are macroscopic with an average particle size of from more than 0.5mm to 2.5mm and that all particles have a particle size within the range of plus or minus 70% of the average particle size.

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Detailed description of the invention

All amount percentages mentioned herein are by weight and based on the total composition unless specifically indicated otherwise.

15

The cleaning compositions of the invention are clear aqueous liquid gels. Thus, all components of the compositions, with the exception of the abrasive particles, are clearly soluble in water. The required viscosity to give the composition its gel consistency is obtained by the addition of suitable thickening agents that are able to give a clear solution.

20

Such thickening agents are known in the art and suitable examples include various vegetable or microbial polysaccharide gums, such as gum arabic, xanthan, alginates and the like, and synthetic polymers e.g. homopolymers of acrylic, methacrylic or maleic acid and copolymers thereof with each other and/or other monomers such as styrene, vinyl ethers etc. such as are marketed by various manufacturers under tradenames such as

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ACUSOL, POLYGEL, CARBOPOL, RHEOVIS and similar products. For the purposes of this invention a gel is considered to be clear if it transmits at least 50% of light at any one wavelength in the visible region i.e. between 400 and 800nm, preferably 550-700nm, measured in a 1cm cuvette in the absence of dyes and abrasive particles. Preferably the

transmittance is at least 70%, more preferably at least 90%.

Gels which are satisfactory for the purposes of the present invention generally have a viscosity of between 100 and 1000 mPas, preferably at least 250 mPas, more preferably 300-750 mPas at 21 sec^{-1} (measured with a Haake viscometer at 20°C). The low shear rate viscosity is such that the gel is able to suspend the macroscopic particles.

10

In many liquid abrasive cleaning products known in the art the required viscosity is obtained by using self-thickening (structuring) mixtures of surfactants often in combination with electrolytes. Although some specific combinations of surfactants under specific circumstances have been disclosed to lead to a transparent or translucent liquid crystal structure, such thickening systems are generally unsuitable for the purposes of the present invention. Most structured surfactant systems cause the liquid to be

20 opaque.

Abrasive particles

In order for the cleaning compositions according to the invention to visually appeal to the consumer the particles are macroscopic, i.e. clearly visible separately to the naked eye. This is in contrast to most abrasive powder particles which generally have average particle size well below 0.3mm and in the vast majority of cases at most 0.1mm (100 μm).

30

Thus, the particles according to the invention have an average particle size between 0.3 and 2.5mm, preferably more than 0.5 and at most 1.5mm. Further, the visual appeal of the compositions is considerably enhanced if the
5 particles are of fairly uniform particle size i.e. they all have a particle size within the range of plus or minus 70% of the average particle size, preferably within a range of $\pm 50\%$, more preferably $\pm 30\%$.

10 The abrasive particles are used in an amount of at least 0.1%, preferably 0.5%. In order to retain the transparent character of the total composition the maximum amount of particles is 20%, preferably 10%, more preferably 5%.

15 The particles may be made of abrasive materials known in the art. Thus, they may consist of granules of one or more of the well known inorganic abrasives such as silica, silicates, calcite and the like. They may consist of polymer granules, such as polyethylene, polypropylene,
20 polycarbonate and the like. Particularly suitable are granules of a biodegradable polymer, such as the starch-derived plastics known in the art.

Alternatively, the abrasive particles may be made of softer
25 materials such as hard waxes and fats, hard fatty acids, hard fatty acid soaps and the like. Such materials may also be mixed with fine particles of any of the known abrasives or with other materials, preferably solid materials, suitable for improving the cleaning process and thereafter
30 formed into granules of the required size.

The visual appeal of the particles, and therefore the total composition, is further enhanced if the particles have a certain minimum sphericity, such that the ratio between the longest and the shortest diameter of a particle in any one direction is at most 3:1, preferably at most 2:1 or even 1.5:1. Particularly preferred are particles with a round, preferably a smooth round shape. Such particles may be made by prilling processes involving making a melt of the particle material, converting it into droplets, which are thereafter cooled in a gas (air) flow. Various processes and suitable equipment therefore are known in the art and may be applied to the organic abrasives, provided they are sufficiently low melting. High melting powders such as inorganic abrasive powders may be made into suitably shaped particles by various agglomeration processes known in the art, if necessary using an agglomeration binder.

Although the cleaning compositions according to the invention may consist of a colourless liquid and solid particles having their natural colour (in many cases white), the compositions are considerably more attractive to the consumer if the liquid and the particles have clearly different colours. They may have different shades of the same colour, e.g. dark blue particles in a light blue liquid, or preferably, the liquid and the particles have contrasting colours e.g. white particles in a blue, green or yellow liquid or vice versa, or coloured particles in a differently coloured liquid.

The pH of the cleaning compositions may vary within wide limits and will generally be between 2 and 14. Certain surfaces are acid-sensitive and for those a composition

with pH of at least 3, preferably 3.5 or even 4 is advised. Improved cleaning of greasy soils is often obtained at alkaline pH i.e. above 7, preferably above 7.5. pH above 12 is generally not required.

5

Surfactants

The compositions according to the invention comprise one or more surfactants which may be chosen from a wide range of
10 anionic, nonionic, cationic, amphoteric and zwitterionic surfactants, examples of which are given below.

A suitable class of anionic surfactants are water-soluble salts of organic sulphuric acid esters and sulphonic acids
15 having in the molecular structure an alkyl group containing 8-22 C atoms or an alkylaryl group containing 6-20 C atoms in the alkyl part.

Examples of such anionic surfactants are water-soluble salts
20 of:

- long chain (i.e. 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;
- 25 - alkylbenzene-sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
- secondary alkanesulphonates.

Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the ethers
30 of fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;

- sulphates of ethoxylated aliphatic alcohols containing 1-8 ethyleneoxy units;
- alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which the alkyl groups contain from 6 to 14 carbon atoms;
- the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali.

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 organic hydrophobic compound which may be aliphatic or alkyl-aromatic in nature. The length of the hydrophilic or polyoxyalkylene chain that 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 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

10

weight and having a molecular weight of from 5,000 to 11,000.

Other classes of nonionic surfactants are:

- 5 - 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 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- 10 - tertiary phosphine oxides of structure $RRRP0$, where one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- 15 - dialkyl sulphoxides of structure $RRS0$ where one R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- 20 - fatty acid alkylolamides;
- alkylene oxide condensates of fatty acid alkylolamides;
- alkyl mercaptans.

Suitable amphoteric surfactants are derivatives of aliphatic
25 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 N-2-hydroxy-dodecyl-N-methyltaurate.

30

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 bromide.

- 5 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
- 10 instance 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium)-propane-1-sulphonate betaine and 3-(cetylmethyl-phosphonium)-ethanesulphonate betaine.
- 15 Further examples of suitable surfactants are compounds commonly used as surface-active agents described 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
- 20 "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.
- 25 Anionic and nonionic surfactants and combinations thereof are particularly preferred. In choosing the (combination of) surfactants care should be taken that they give a clear solution. Hydrotropes such as Na xylene- or cumene-sulfonate or others known in the art may be added if
- 30 necessary.

The surfactants are generally present in an amount of at least 0.1%, but below 15%, preferably 0.5-10%, more preferably at least 1.0%.

5

Optional components

The compositions according to the invention may contain various optional components well known in the art which
10 improve cleaning performance or consumer appeal. Thus, the compositions may contain builders, chelating agents, electrolytes, organic solvents, active halogen or peroxy bleaching agents, pH regulating agents, anti-foams, antimicrobials, preservatives, perfumes, insect repellents,
15 etc.

The process

20 The process for cleaning a hard surface involves applying to the hard surface a suitable amount of the composition according to the invention, generally followed by rubbing the composition over the surface to be cleaned using a wipe or cloth. The composition may be applied directly to the
25 surface or, alternatively, the composition may be applied to the (preferably damp) wipe or cloth first and thereafter this is rubbed over the surface with the side on which the composition was applied facing the surface. In case the abrasive particles are made of polymer or other relatively
30 soft material the compositions according to the invention are very suitable for cleaning delicate surfaces which would otherwise easily be scratched.

Example 1

A clear liquid blue coloured gel was prepared, according to
 5 the formula below, which contained fatty acid granules
 having a diameter of 0.8 mm $\pm$ 20% dispersed therein.

INGREDIENT	TRADE NAME	SUPPLIER	LEVEL In %
Phosphoric Acid			0.050
Nonionic	Neodol 91.8	Condea DAC	3.000
Polymer	Carbopol 2623	Goodrich	0.280
Silicon	DB31		0.003
Nonionic	Neodol 91.5	Condea DAC	2.000
Sodium bicarbonate	Baking Soda	Solvay	0.100
Preservative	Proxel GXL	Zeneca	0.020
Fatty acid granule	Simiol 60	Unigema	1.000
NaOH to pH 8.0			0.110
Perfume			0.270
Blue colourant	Blu Patent	Fiori	0.0006
Demin water		to	100

10 Example 2

A clear liquid green coloured gel was prepared, according
 to the formula below, which contained polyethylene granules
 having a diameter of 0.8 mm $\pm$ 20% dispersed therein.

15 The product had a viscosity of 380 mPas at 21 sec⁻¹ and 20°C
 and a pH of 11.

INGREDIENT	TRADE NAME	LEVEL in %
Xanthan gum	Kelzan ST	0.50
Diphosphonic acid	Dequest 2010	0.75
NaOH		1.20
Nonionic C12-C15 7EO	Dobanol 23 6.5	3.30
IAS acid		1.72
Di-ethylene glycol mono-butyl ether	Butyl Digol	2.00
Fatty acid	Prifac 7907	0.09
Colourant	Blu Patent V	
Perfume		0.50
Polyethylene granules	AC 316	1.00
Demin water	to	100.

Example 3

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A mildly acidic (pH around 4.5) hydrogen peroxide containing clear hard surface cleaning gel was prepared according to the formula below. Fatty acid prills containing 10% by weight (calculated on the prills) sodium bicarbonate and having a diameter of 1.0 mm $\pm$ 20% were dispersed therein.

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INGREDIENT	TRADE NAME	LEVEL in %
Sequestrant	Dequest 2046	0.10
Nonionic	Lialet 111-5.5EO	2.00
	Dobanol 91 8EO	5.00
Fatty acid (in solution)		0.30
Polyacrylate polymer	Carbopol ETD2623	0.30
Hydrogen peroxide		3.00
Citric acid	(buffer)	0.08
Sodium hydroxide		as required
Dye		
Perfume		
Fatty acid prills		2.0

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or

5 steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived

10 from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

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The Claims defining the invention are as follows:

1. Clear aqueous gel liquid abrasive hard surface cleaning composition comprising one or more detergent surfactants and 0.1 to 20 wt% abrasive particles
 5 characterised in that the abrasive particles dispersed in the liquid are macroscopic with an average particle size of from more than 0.5mm to 2.5mm and that all particles have a particle size within the range of plus or minus 70% of the average particle size.
- 10 2. Cleaning composition according to claim 1 characterised in that the average particle size is at most 1.5mm.
3. Cleaning composition according to claim 1 or claim 2 characterised in that all particles have particle size within the range of $\pm 50\%$ of the average particle size.
- 15 4. Cleaning composition according to any one of claims 1-3 characterised in that the particles have sphericity, such that the ratio between the longest and the shortest diameter of a particle in any one direction is at most 3:1.
- 20 5. Cleaning composition according to claim 4 characterised in that the particles have a smooth round shape.
6. Cleaning composition according to any one of claims 1-5 characterised in that it has a viscosity of between 100 and 1000 mPas at 21 sec⁻¹.

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7. Cleaning composition according to any one of claims 1-6 characterised in that the liquid and the particles have different colours.
8. Cleaning composition according to claim 7 characterised in that the liquid and the abrasive particles have contrasting colours.
9. Cleaning composition according to any one of claims 1-8 characterised in that it contains at least 0.1 but less than 15% surfactant.
10. Cleaning composition according to any one of claims 1-9 characterised in that the surfactant is chosen from anionic surfactants, nonionic surfactants and mixtures thereof.
11. Process for cleaning a hard surface comprising the step of applying to the surface a cleaning composition according to any one of claims 1-10.
12. A clear aqueous gel liquid abrasive hard surface cleaning composition substantially as hereinbefore described with reference to the examples.

DATED this 26th day of April 2006.

UNILEVER PLC

By Its Patent Attorneys

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