(11) Application No. AU 199647893 B2 (12) PATENT (10) Patent No. 719466 (19) AUSTRALIAN PATENT OFFICE (54)Cleaning composition comprising saturated dialkyl cationic surfactants (51) <sup>6</sup> International Patent Classification(s) C11D 001/835 (21) Application No: (22) Application Date: 199647893 1996 .02 .07 WIPO No: w096/26257 (87) (30)Priority Data (33) (32) Date (31) Number Country GB 1995 .02 .23 9503594 (43)Publication Date : 1996 .09 .11 Publication Journal Date : 1996 .10 .31 (43)(44)Accepted Journal Date : 2000 .05 .11 (71) Applicant(s) Unilever PLC (72)Inventor(s) Matthew James Leach (74)Agent/Attorney DAVIES COLLISON CAVE,1 Little Collins Street, MELBOURNE VIC 3000 (56)Related Art US 4065409 WO 94/06899

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### (54) Title: CLEANING COMPOSITION COMPRISING SATURATED DIALKYL CATIONIC SURFACTANTS

#### (57) Abstract

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The specification discloses improved compositions which both clean a surface and are believed to deposit thereupon a layer of cationic surfactant which assists the release of soil subsequently deposited upon the said surface. These comprise a surfactant mixture, wherein said surfactant mixture itself comprises: a) at least 65 % wt on total surfactant of nonionic surfactant; b) less than 1 % wt on total surfactant of anionic surfactant; and c) 0.1-35 % wt on total surfactant of a cationic surfactant which is a substantially ethylenically saturated dialkyl quaternary ammonium compound.

# CLEANING COMPOSITION COMPRISING SATURATED DIALKYL CATIONIC SURFACTANTS

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#### Technical Field

The present invention relates to a cleaning composition for hard surfaces, wherein said composition comprises both a fully saturated dialkyl cationic surfactant and a nonionic surfactant.

#### Background to the Invention

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In traditional cleaning of hard surfaces such as wood, glazed tiles, painted metal and the like, it is known to follow soil removal using surfactant or solvent based compositions with the application of a lacquer, wax or polish as a separate operation so as to seal and protect the surface and reduce the rate of soil redeposition. This two-step cleaning and sealing operation is time-consuming and complex.

- It is known to incorporate components into a surfactantbased composition with the intention that deposition of such components onto surfaces will provide a protective layer in a one step cleaning operation.
- 30 GB 1528592 (1978) discloses alkaline, floor cleaning compositions which comprise an organic, polycarboxylic acid co-polymer having a molecular weight in the range 100,000-2,500,000 which is soluble in aqueous solutions having a pH of 8.5 or above. These polymers are readily available in commercial quantities.

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GB 1534722 (1978) discloses granular hard surface cleaning compositions which comprise surfactant and, as "a soil removal improvement mixture", a polyvinyl alcohol or pyrrolidone and a biopolysaccharide. These polymers have molecular weights ranging from around 5000 to around 360,000 and are available in industrially useful quantities. The compositions form alkaline solutions.

US 07/297807 (EP379256), as described in EP 0467472 A2 (Colgate Palmolive) demonstrates that the incorporation of 2.3% of a 15-20% aqueous solution of the cationic polymer poly-[beta(methyl diethyl-ammonium) ethyl-methacrylate] in a mixed nonionic surfactant system for hard surface cleaning results in significant improvement of ease of subsequent re-cleaning of previously soiled and cleaned ceramic tiles.

EP 0467472 A2 discloses that soil release promoting polymers such as, but not limited to, the cationic poly-[beta(methyl diethyl-ammonium) ethyl-methacrylate] are also effective in combination with anionic and cationic surfactant. In that published application it is stated that 'said adsorbed polymer forms a residual anti-soiling hydrophillic layer of said soil release promoting polymer on said surface, whereby removal of soils subsequently deposited thereupon requires less work than in the absence of said residual layer'. The molecular weight range of the polymers falls into the range 4,000-100,000 although the use of polymers having a molecular weight above 50,000 is discouraged for solubility reasons.

EP 0379256 discloses similar compositions to the above-mentioned document, having up to 2%wt of an optional quaternised, anti-static, polymer of molecular weight in the range of 2,000 - 500,000, and being characterised by an



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acidic pH of 2-4 and a 2-4%wt of a nonionic surfactant system. Specific examples relate to compositions having a



pH of 2.5 and comprising 2.2%wt of a mixed nonionic system and 0.07% of the specified cationic polymer. The modified polymer is again said to function as a soil release agent.

5 US-A-4065409 discloses a detergent mixture for cleaning hard surfaces which comprises a low level of nonionic detergent (which can include ethoxylated alcohol) and a quat. (such as dimethyl didecyl ammonium chloride: DDAC). There is no mention of any soil release benefit in this document.

WO-A-8605199 discloses compositions which comprise glycoside nonionics. It is noted that the compositions of the prior art disclosed in this citation are said to leave essentially no residues on the surface and it is believed that the compositions of the reference are also intended to leave no residues.

WO-A-9406899 also discloses compositions which comprise
quaternised mono and di tallow acid esters in combination
with glycoside nonionics

In addition to the above it is known from US 4606842 to use low molecular weight polyacrylic resins as a builder in glass cleaning compositions of the spray-on, wipe-off type. Baker et al in US 4690779 discloses the use of the combination of polymers of polyacrylic acid having a molecular weight below 5000 with certain nonionic surfactants in hard surface cleaning compositions. The primary function of the polymer in these systems is as a builder.

From the above it can be seen that it is known to include certain polymers in generally alkaline hard surface cleaning compositions with so as to obtain either a primary cleaning benefit when the composition is first used on the

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surface or a secondary cleaning benefit by modification of the surface so as hinder soil deposition or otherwise facilitate repeated cleaning.

Some attention has been paid to other surface treatment agents, including specific cationic detergents. WO 91/09930 (Ques Industries) discloses the use 'ETHOQUAT' (TM) on aluminium e.g. metal surfaces such as those found on vehicles.

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#### Brief Description of the Invention

We have devised improved compositions which both clean a surface and are believed to deposit thereupon a layer of cationic surfactant which assists the release of soil subsequently deposited upon the said surface.



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Accordingly the present invention provides an aqueous, hard-surface cleaning composition comprising a surfactant mixture, wherein said surfactant mixture comprises:

An aqueous, hard-surface cleaning composition comprising a surfactant mixture, wherein said surfactant mixture comprises:

a) at least 65%wt on total surfactant of nonionic surfactant chosen from condensates of aliphatic alcohols having 6-22 carbon atoms with ethylene oxide and condensates of alkylphenols having an alkyl group of 6-12 carbon atoms with 5-25 moles of ethylene oxide per mole of alkyl phenol,

b) less than 1%wt on total surfactant of anionic surfactant, and,  $\frac{i}{k}$ 

c) 0.1-35%wt on total surfactant of a ethyleneically saturated dialkyl cationic surfactant which contain at least two alkyl groups of at least 8 carbon atoms long and which are chosen from:

I compounds of the general formula:

$$X^{-}$$
 $R2-N^{+}-(CH_{2})_{n}-CH-(CH_{2})_{m}-OOCR_{5}$ 
 $R3/$ 
 $OOCR_{4}$ 

wherein  $R_1$ ,  $R_2$  and  $R_3$  are independently  $C_{1-6}$  alkyl or hydrogen, n and m are 0-4,  $00CR_4$  and  $00CR_5$  are fatty acid residues comprising 8-26 carbon atoms and X is a monovalent anion equivalent

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- II compounds of the general formula:
- $X^{-}$  [CH<sub>3</sub> (CH<sub>2</sub>)<sub>n</sub>CO.NH (CH<sub>2</sub>)<sub>m</sub>]<sub>2</sub>.N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is an monovalent anion equivalent.

- III compounds of the general formula:
- $X^{-}$  [CH<sub>3</sub> (CH<sub>2</sub>)<sub>n</sub>COO (CH<sub>2</sub>)<sub>m</sub>]<sub>2</sub>.  $N^{+}R_1R_2$

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is an monovalent anion equivalent.

## Detailed Description of the Invention

A range of cationic dialkyl quaternary ammonium compounds find useful application in the compositions of the present invention. While these can contain moieties such as C=O the alkyl chains are free of moieties such as C=C, i.e. they are ethyleneically saturated. Moreover, while it is important that the molecules contain at least two moderately long alkyl chains the compounds can have more than two of said alkyl chains. In the context of the present invention at least two of these alkyl groups are or more carbons long.



Typically the cationic surfactant is of the general formula:

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$$\begin{array}{c} R1 \ \backslash \\ X^{-}R2-N^{+}-(CH_{2}) \stackrel{\cdot}{n}-CH-(CH_{2}) \ m-OOCR_{5} \\ R3 \ / \\ OOCR_{4} \end{array}$$

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wherein  $R_1$ ,  $R_2$  and  $R_3$  are independently  $C_{16}$  alkyl or hydrogen, n and m are 0-4, OOCR<sub>4</sub> and OOCR<sub>5</sub> are fatty acid residues comprising 8-26 carbon atoms and X is a

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monovalent anion equivalent. More typically, the cationic surfactant comprises a cation of the formula given above wherein m=1 and n=1.

Preferably, the cationic surfactant comprises a cation of the formula given above wherein  $R_1=R_2=R_3=CH_3$ . Most preferably the cationic surfactant comprises a cation of the formula given above wherein  $R_4$  and  $R_5$  are independently  $C_{12}-C_{20}$ .

Alternative fully saturated dialkyl quaternary ammonium compounds include

 $X^{-}$  [CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>CO.NH(CH<sub>2</sub>)<sub>m</sub>]<sub>2</sub>.N\*R<sub>1</sub>R<sub>2</sub>

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is an monovalent anion equivalent.

Preferably R<sub>1</sub> is methyl, R<sub>2</sub> is - (CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>H, or methyl.

Further fully saturated dialkyl quaternary ammonium compounds include

 $X^{-}$  [CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>COO(CH<sub>2</sub>)<sub>m</sub>]<sub>2</sub>. N'R<sub>1</sub>R<sub>2</sub>

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is an monovalent anion equivalent.

Preferably  $R_1$  is methyl,  $R_2$  is  $-(CH_2CH_2O)_xH$  (where x is on average 1-2), or methyl, and m is 2.

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Further fully saturated dialkyl quaternary ammonium compounds include

 $X^{-}[CH_{3}(CH_{2})_{n}]_{2}.N^{+}R_{1}R_{2}$ 

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wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene glycol residues or polymers thereof, n is 8-26 and X is an monovalent anion equivalent. Preferably  $R_1$  is methyl,  $R_2$  is -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>H (where x is 1-2), or methyl. Preferably n is selected such that the longer alkyl chains have a chain length distribution similar to that of tallow.

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The pH of the compositions according to the present invention is acidic, alkaline or neutral.

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Typical compositions according to the present invention have a pH of less than 7.5 where ester groups are used. Where ester groups are absent as linkages in the cationic surfactant the pH can be higher than 7.5.

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A preferred cationic surfactant is:

[(CH<sub>1</sub>)<sub>3</sub>N-CH<sub>2</sub>-CH (OOCR<sub>4</sub>)-CH<sub>2</sub>OOCR<sub>5</sub> +X

wherein,  $R_4$  and  $R_5$  are independently  $C_{12}$ - $C_{20}$  and the composition is essentially free of anionic surfactant. Materials falling within this general class are available from Hoechst. Most preferably,  $R_4$  and  $R_5$  are fatty acid residue alkyl chains having a chain length distribution corresponding to that of tallow.

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Another preferred cationic is:

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 $X^{-}$  [CH<sub>3</sub> (CH<sub>2</sub>) CO.NH(CH<sub>2</sub>) , N'R<sub>1</sub>R<sub>2</sub>



wherein n is 11-19,  $R_1$  is methyl and  $R_2$  is -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub> (where x is 1-2), H, or methyl. Materials falling within this general description are available in the marketplace as ACCOSOFT 440/75 (TM) from Stepan.

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In the above-mentioned formulations it is preferable that the ethoxylation number x is close to 1.7, i.e. 1.5-2.0.

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It is believed that the cationic surfactants present in the compositions of the present invention modify the surface energy of surfaces to which the composition is applied so as to raise the contact angle of soil subsequently deposited on the modified surface. Preferred cationics have a marked effect on the contact angle of test liquids which are applied to surfaces which have been treated with said cationics. Thus, for glass microscope slides which has been untreated the contact angle of a 10 microlitre dodecane droplet is less than 10 degrees. When treated with a composition embodying the present invention, i.e. an aqueous solution of 5% nonionic and 1% cationic, as described in further detail below: the contact angle of the dodecane droplet is increased to typically above 20

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degrees.

Accordingly, the present invention also extends to a method for cleaning a hard surface with a net negative charge which comprises the step of treating said surface with a composition as described herein.

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It is essential that the compositions of the present invention comprise an alkoxylated alcohol nonionic surfactant. The presence of nonionic surfactant is believed to contribute significantly to the cleaning effectiveness of the compositions of the invention.

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Suitable nonionic detergent active compounds can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophillic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature.

The length of the hydrophillic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophillic and hydrophobic elements.

Particular examples include the condensation product of aliphatic alcohols having from 6 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol and 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.



Particularly preferred nonionic surfactants are the ethoxylated alcohols having 6-14 carbons and 2-9 moles of ethoxylation. Suitable materials include IMBENTIN 91/35 OFA (TM), a  $C_{10}$  nonionic having on average five moles of ethoxylation.

Many more nonionic surfactants produced by condensation of alkylene oxides with aliphatic or alkylaromatic compounds are known to the skilled worker, as set forth in M. J. Schick 'Nonionic Surfactants', Marcel Dekker (1967) and subsequent editions of the same work.

The amount of nonionic detergent active to be employed in the composition of the invention will generally be from 1 to 30%wt, preferably from 2 to 20%wt, and most preferably from 5 to 10%wt.

It is particularly preferred that the ratio of nonionic surfactant to anionic and cationic surfactant ts such that > 75% of the total surfactant present in the composition is nonionic.

It is essential that the compositions of the present invention only comprise low levels of anionic detergent actives or that these actives are absent in so far as is practical. It is believed that the presence of anionic detergents will cause the formation of a complex between the cationic and anionic detergents which will reduce the effectiveness of the compositions.

30 The overall surfactant content of compositions according to the present invention will generally be 1 to 30%.

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Hydrophobic oils are optional components of compositions according to the present invention. Suitable oils include oils which rapidly dissolve triglyceride. When oils are present preferred oils include limonene, para-cymene, dibutyl ether and butyl butyrate.

The composition according to the invention can contain other ingredients which aid in their cleaning performance.

For example, the composition can contain detergent 10 builders. Suitable builders include materials such as carbonates and bicarbonates, nitrilotriacetates, polycarboxylates, citrates, dicarboxylic acids, watersoluble phosphates especially polyphosphates, mixtures of ortho- and pyrophosphate, zeolites and mixtures thereof. 15 Such builders (particularly the phosphates and the carbonates) can additionally function as abrasives if present in an amount in excess of their solubility in water: although it is preferable that the compositions of the present invention are essentially free of abrasive 20 particles. In general, the builder, will form from 0.1 to 25% by weight of the composition.

Metal ion sequestrants such as

ethylenediaminetetraacetates, amino-polyphosphonates

(DEQUEST<sup>R</sup>) and phosphates and a wide variety of other polyfunctional organic acids and salts, can also optionally be
employed.

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

Examples of suds regulating materials are organic solvents, hydrophobic silica and silicone oils or hydrocarbons.

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Solvents are optional components of compositions according to the present invention. Where solvents are present, preferred solvents are of the form  $R_1\text{-}0\text{-}(E0)_m\text{-}(P0)_n\text{-}R_2$ , wherein  $R_1$  and  $R_2$  are independently C2-6 alkyl or H, but not both hydrogen, m and n are independently 0-5. More preferably, the solvent is selected from the group comprising di-ethylene glycol mono n-butyl ether, monoethylene glycol mono n-butyl ether, monoethylene glycol mono n-butyl ether, propylene glycol n-butyl ether, isopropanol, ethanol, butanol and mixtures thereof. Alternative solvents include the pyrrolid(in)ones, for example N-methyl pyrrolidinone.

Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as pH regulants, colourants, optical brighteners, soil suspending agents, detersive enzymes, compatible bleaching agents, gel-control agents, freeze-thaw stabilisers, bactericides, preservatives, detergent hydrotropes, perfumes and opacifiers.

In embodiments where the cleaning of burnt on or otherwise crosslinked soils is envisaged, it is particularly preferred that the composition comprises 1-10% of an alkanolamine, with levels of 2-6%wt being particularly preferred. Particularly suitable alkanolamines include: 2-amino-2-methyl-1-propanol(AMP), mono-ethanolamine and diethanolamine.

We have determined that it is particularly advantageous to include a polymer in the compositions of the present invention so as to reduce the level of formation of exceptionally fine droplets when the composition is sprayed as a relatively fine mist. Suitable polymers include polyvinyl pyrrolidone, available in the marketplace as Polymer PVP K-90.



Suitable levels of PVP polymer range upwards from 50ppm. Levels of 300-2000ppm are particularly preferred.

While the compositions of the present invention can be alkaline, acidic or neutral, it is preferred for kitchen soils that the compositions are generally alkaline, having a preferred pH >6.

Particularly preferred compositions have a pH of >10 and comprise, in admixture with water,:

- a) 3-15% alkoxylated alcohol nonionic surfactant (preferably, C9-C12 EO5-8 nonionic surfactant)
- b) 2-10% solvent (preferably, diethylene glycol mono-nbutyl ether)
- c) 2-6% alkanolamine (preferably, 2-amino-2-methyl-1-propanol)
- d) 0-5% buffer/alkali (preferably, an alkali metal carbonate),
- e) 0-2000ppm polymer (preferably, PVP), and
- f) 0.1-2% of a cationic surfactant comprises a cation of the general formula:

 $X^{-}$  [CH<sub>3</sub> (CH<sub>2</sub>)  $_{n}$ CO, NH (CH<sub>2</sub>)  $_{m}$ ]  $_{2}$ . N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is an monovalent anion equivalent, said composition being packaged in a container adapted to produce a spray of 0.1-



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1.5ml of product per spraying operation, said spray having an average drop size in the range 30-300 microns.

In order that the present invention may be better

understood it will be described hereinafter by way of example.

#### EXAMPLES

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Aqueous compositions comprising nonionic surfactant, and a relatively low level of cationic surfactant were prepared as in Tables 1 and 2 below: using the following materials (all compositions are given in terms of wt% unless otherwise stated):

NONI:

IMBENTIN 91/35 OFA (TM),

CIAB:

Cetyl trimethyl ammonium bromide,

HEQ:

[ (CH<sub>3</sub>)<sub>3</sub>N-CH, OOCR<sub>4</sub>-CH<sub>2</sub>. OOCR<sub>5</sub> ] <sup>+</sup>Cl<sup>-</sup> wherein OOCR<sub>4</sub>

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and OOCRs are fatty acid residues having a

fatty acid chain length corresponding to

tallow (manufactured by Hoechst).

ACCO:

ACCOSOFT 440/75 ex. Stepan.

AMP:

amino-2-methyl-1-propanol

digol:

Butyl Digol (TM)

The compositions were prepared at room temperature by mixing except where HEQ and ACCO were used, these latter material being dissolved in three parts propylene glycol at 70 celcius and added to water, also at 70 celcius, while stirring.

Results 'ETh' and 'EPh' are explained below. CTAB, a typical mono-alkyl cationic surfactant was selected as a control as it has a significantly lower effect on the

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contact angle of a dodecane droplet placed on a glass (microscope) slide which has been treated with a 1%

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solution of the dialkyl cationic in a 5% aqueous solution of NONI.

The surface energy gamma,/mN.m<sup>-1</sup> of the CTAB treated glass (microscope slide) surface is believed to be of the order of 25 mN.m<sup>-1</sup> (as measured by the method of Grifalco, Good, Fowkes and Young (see Physical chemistry of Surfaces, A. A. Adamson, Wiley, New York [1990])), whereas the surface energy of surfaces treated with similar solutions of the cationics used in the compositions of the present invention was less than 25 mN.m<sup>-1</sup>.

TABLE 1

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EXAMPLE:					
Comp:	1	2	3	4	5
NONI	5%	5%	5%	5%	5%
CTAB	_	1%	_	-	<u> </u>
HEQ	_	_	.01%	0.1%	1/0%
ETh	*	*	*	2140	2119
EPh	2634	1697		896	776
	<del></del>	<del> </del>	+		

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Gamma,

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\* indicates that the tile was not clean in less than 2 minutes i.e. the cleaning effort was believed to be of the order of 10000 Ns.

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#### Table 2

Example						
Comp:	6	7	8	9 .		
NONI	10%	10%	10%	10%		
AMP	4%	48	4%	4%		
K <sub>2</sub> C0,	1.2%	1.2%	1.2%	1.2%		
Digol	88	8%	88	8%		
Prop G		-	0.6%	3.0%		
CTAB	-	1%	<u>-</u>			
ACCO	_	-	0.2%	1.0%		
ETh	930	469	189	137		

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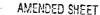
100g dehydrated castor oil (ex. UNICHEMA) was weighed into a glass jar. To this was added 0.2g Fat Red (TM) dye (ex. SIMGA) and the mixture was stirred vigorously (2000 RPM) for 6 hours using a Heidolph stirrer. The stirred mixture was refrigerated when not in use.

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Vitreous enamel times (380x300mm) were cleaned using a fresh damp J-CLOTH (TM) using, in sequence, JIF LAC (TM), a commercially available brand of hand dishwashing liquid and calcite powder. After drying residual calcite was removed by buffing with a paper towel.

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1ml of the compositions listed in Table 1 was wiped onto the cleaned tiles using a fresh damp J-CLOTH. The tiles were rinsed with tap water for 15 seconds to remove excess composition and allowed to drain. Tiles were soiled over a 215x150mm area using a DeVilbiss (TM) gravity feed spray gun (MODEL MPS-514/515) using compressed air at 25 psi, by spraying from 27 cm for 35 seconds. The soiled tiles were either laid horizontally in an oven at 85 Celcius and



thermally aged for 2 hours and then stored overnight, or aged photochemically by exposure to daylight for 3-6 days. Tiles were cleaned by hand using damp J-cloths and for the examples cited in table 1, 1-2 ml of a control composition which comprised the formulation given in table 3 below:

## Table 3 control formulation

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5%	NONI
3.4%	AMP
0.2M	K <sub>2</sub> CO <sub>3</sub>
5%	N-methyl pyrollidon

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The effort required to clean the tiles was determined as 20 'ETh' in table 1 for thermally aged tiles and 'EPh' for photochemically aged tiles.

2ml of the compositions listed in Table 2 were wiped onto the cleaned tiles using a fresh damp J-CLOTH. The tiles were soiled and aged as described above and cleaned with same formulation as used in pre-treatment rather than the control formulation.

From the results presented in tables 1 and 2 it can be seen that the compositions according to the present invention, show a marked reduction in the cleaning effort required as compared with comparable compositions which either contain no cationic surfactant or contain a cationic surfactant which is not a saturated dialkyl cationic.

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The claims defining the invention are as follows:

- An aqueous, hard-surface cleaning composition comprising a surfactant mixture, wherein said surfactant mixture comprises:
  - a) at least 65%wt on total surfactant of nonionic surfactant chosen from condensates of aliphatic alcohols having 6-22 carbon atoms with ethylene oxide and condensates of alkylphenols having an alkyl group of 6-12 carbon atoms with 5-25 moles of ethylene oxide per mole of alkyl phenol,
  - b) less than 1%wt on total surfactant of anionic surfactant, and,
  - c) 0.1-35%wt on total surfactant of a ethyleneically saturated dialkyl cationic surfactant which contain at least two alkyl groups of at least 8 carbon atoms long and which are chosen from:
    - I compounds of the general formula:

$$X^{-}$$
 $R2-N^{+}-(CH_{2})_{n}-CH-(CH_{2})_{m}-OOCR_{5}$ 
 $R3/$ 
 $OOCR_{4}$ 

wherein  $R_1$ ,  $R_2$  and  $R_3$  are independently  $C_{1-6}$  alkyl or hydrogen, n and m are 0-4, OOCR<sub>4</sub> and OOCR<sub>5</sub> are fatty acid residues comprising 8-26 carbon atoms and X is a monovalent anion equivalent.



II compounds of the general formula:

 $X^{-}$  [CH<sub>3</sub> (CH<sub>2</sub>)<sub>n</sub>CO.NH (CH<sub>2</sub>)<sub>m</sub>]<sub>2</sub>.  $N^{+}$ R<sub>1</sub>R<sub>2</sub>

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is an monovalent anion equivalent.

III compounds of the general formula:

 $X^{-}$  [CH<sub>3</sub> (CH<sub>2</sub>)<sub>n</sub>COO (CH<sub>2</sub>)<sub>m</sub>]<sub>2</sub>.N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is an monovalent anion equivalent.

- Composition according to claim 1 comprising 1-30%wt total surfactant.
- 3. Composition according to claims 1 or 2 wherein the saturated dialkyl cationic surfactant is a compound of the general formula:

 $X^{-}$  [CH<sub>3</sub> (CH<sub>2</sub>)<sub>n</sub>CO.NH (CH<sub>2</sub>)<sub>m</sub>]<sub>2</sub>.N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene



glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is a monovalent anion equivalent.

- 4. Composition according to claim 3 wherein the cationic surfactant comprises a cation wherein m=1 and n=1 and  $R_1=R_2=R_3=CH_3$ .
- 5. Composition according to claims 1 or 2 wherein the saturated dialkyl cationic surfactant is a compound of the general formula:

$$X^{-}$$

R1\
R2-N^{+}-(CH<sub>2</sub>)<sub>n</sub>-CH-(CH<sub>2</sub>)<sub>m</sub>-OOCR<sub>5</sub>
R3/
OOCR<sub>4</sub>

wherein  $R_1$ ,  $R_2$  and  $R_3$  are independently  $C_{1-6}$  alkyl or hydrogen, n and m are 0-4,  $R_4COO$  and  $R_5COO$  are fatty acid residues comprising 8-26 carbon atoms and X is a monovalent anion equivalent.

- 6. Composition according to claim 5 wherein the cationic surfactant comprises a cation wherein  $R_1$ =  $CH_3$  and  $R_2$  =  $(CH_2CH_2O)_xH$  or  $CH_3$ .
- 7. Composition according to claims 1 or 2 wherein the saturated dialkyl cationic surfactant is a compound of the general formula:

$$X^{-}$$
 [CH<sub>3</sub> (CH<sub>2</sub>)<sub>n</sub>COO (CH<sub>2</sub>)<sub>m</sub>]<sub>2</sub>.  $N^{+}R_1R_2$ 

wherein  $R_1$  and  $R_2$  are independently selected from hydrogen, C1-C4 alkyl, C1-C4 hydroxy alkyl and alkylene  $\,$ 



glycol residues or polymers thereof, n is 8-26 and m is 1-4 and X is a monovalent anion equivalent.

- 8. Composition according to claim 7 wherein  $R_1$  is methyl,  $R_2$  is  $-(CH_2CH_2O)_xH$  (where x is on average 1-2) or methyl and m is 2.
- Composition according to claims 1-8 further comprising,
   1-10% of an alkanolamine.
- 10. Composition according to claims 1-9 which is essentially free of anionic surfactant.
- 11. Composition according to claims 1-10 having a pH >6.
- 12. Composition according to claims 1-11 further comprising, a builder selected from the group comprising carbonates and bicarbonates, nitrilotriacetates, polycarboxylates, citrates, dicarboxylic acids, water-soluble phosphates especially polyphosphates, mixtures of ortho- and pyrophosphate, zeolites and mixtures thereof.
- 13. Method for cleaning a hard surface with a net negative charge which comprises the step of treating said surface with a composition according to any of the preceding claims.
- 14. Aqueous, hard-surface cleaning compositions or methods involving/containing same, substantially as hereinbefore described with reference to the Examples.

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UNILEVER PLC

By its Patent Attorneys

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