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(54) Antimicrobial hard surface cleaner

(57) The invention provides an aqueous, antimicrobial hard surface cleaner with significantly improved residue removal and substantially reduced filming/streaking, said cleaner comprising:

(a) an effective amount of a solvent selected from C_{1-6} alkanol, C_{3-24} alkylene glycol ether, and mixtures thereof;

(b) an effective amount of a surfactant selected from amphoteric, nonionic surfactants, and mixtures thereof;

(c) an effective amount of a quaternary ammonium surfactant;

(d) an effective amount of a builder; and

(d) the remainder as substantially all water.

EP 0 691 397 A2

Description

The invention relates to a non-rinse, isotropic, antimicrobial hard surface cleaner especially adapted to be used on glossy or smooth, hard surfaces, which removes soils deposited thereon and disinfects same, while significantly reducing the amount of residue caused by unremoved soil, cleaner, or a combination thereof.

Cleaning hard, glossy surfaces has proven to be problematic. To remove soils deposited on such surfaces, the typical approach is to use an alkaline ammonium-based aqueous cleaner or other aqueous cleaners containing various mixtures of surfactants and other cleaning additives. Unfortunately, many of the ammonia-based cleaners have fairly poor soil removing ability, while many of the surfactant-based cleaners leave fairly significant amounts of residue on such hard, glossy surfaces. This residue is seen in the phenomena of streaking, in which the soil, cleaner, or both are inconsistently wicked off the surface. and filming, in which a thin layer of the residue actually clings to the surface desired to be cleaned.

Additionally, quaternary ammonium based liquid hard surface cleaners are in common use, typically as bathroom cleaners. Certain quaternary ammonium compounds can be effective as antimicrobial agents in small dosages in these cleaners. However, these types of cleaners typically are not effective on glossy, hard surfaces because they tend to leave a visible residue.

Baker et al., U.S. Patent 4,690,779, demonstrated a hard surface cleaner having improved non-streaking/filming properties in which a combination of low molecular weight polymer (e.g., polyethylene glycol) and certain surfactants were combined.

Corn et al., E.P. 0393772 and E.P. 0428816, describe hard surface cleaners containing anionic surfactants with ammonium counterions, and additional adjuncts.

G.B. 2,160,887 describes a cleaning system in which a combination of nonionic and anionic surfactants (including an alkanolamine salt alkyl sulfate) is contended to enhance cleaning efficacy.

WO 91/11505 describes a glass cleaner containing a zwitterionic surfactant, monoethanolamine and/or beta-aminoalkanols as solvents/buffers for assertedly improving cleaning and reducing filming spotting.

A series of patents to Flanagan (U.S. 4,065,409, U.S. 4,174,304, U.S. 4,203,872 and U.S. 4,264,304) describe dilutable cleaner concentrates which included quaternary ammonium surfactants. The compositions of these inventions do not claim improved filming/streaking properties.

Thus, the prior art hard surface cleaners fail to achieve the desired goals of reduced residue (streaking and/or filming) and antimicrobial action.

The invention provides an aqueous, antimicrobial hard surface cleaner with significantly improved residue removal and substantially reduced filming/streaking, said cleaner comprising:

(a) an effective amount of a solvent selected from C_{1-6} alkanol, C_{3-24} alkylene glycol ether, and mixtures thereof;

(b) an effective amount of a surfactant selected from amphoteric, nonionic surfactants, and mixtures thereof;

(c) an effective amount of a quaternary ammonium surfactant;

(d) an effective amount of a builder; and

(e) the remainder as substantially all water.

The invention further comprises a method of cleaning soils from hard surfaces by applying said inventive cleaner to said soil, and removing both from said surface, while disinfecting said surface.

It is therefore an object of this invention to improve soil removal from hard surfaces.

It is another object of this invention to disinfect hard surfaces while improving soil removal performance.

It is another object of this invention to reduce filming which results from a residue of cleaner, soil, or both remaining on the hard surface intended to be cleaned.

It is a further object of this invention to reduce streaking, which results from inconsistent removal of the cleaner, soil, or both, from the hard surface intended to be cleaned.

The invention is an improved cleaning, substantially non-streaking/filming, antimicrobial hard surface cleaner especially adapted to be used on glossy or smooth, hard surfaces. The cleaner benefits from the presence of a quaternary ammonium surfactant which contributes unexpectedly to both antimicrobial efficacy as well as to the complete removal of soils and the cleaner from the surface being cleaned. The cleaner itself has the following ingredients:

(a) an effective amount of a solvent selected from C_{1-6} alkanol, C_{3-24} alkylene glycol ether, and mixtures thereof;

(b) an effective amount of a surfactant selected from amphoteric, nonionic surfactants, and mixtures thereof;

(c) an effective amount of a quaternary ammonium surfactant; and

(d) an effective amount of a builder; and

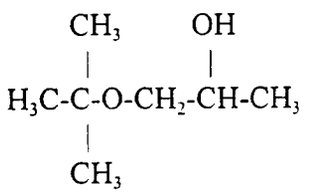
(e) the remainder as substantially all water.

Additional adjuncts in small amounts such as fragrance, dye and the like can be included to provide desirable attributes of such adjuncts.

In the application, effective amounts are generally those amounts listed as the ranges or levels of ingredients in the descriptions which follow hereto. Unless otherwise stated, amounts listed in percentage ("%'s") are in weight percent of the composition, unless otherwise noted.

The solvent is selected from C_{1-6} alkanol, C_{3-24} alkylene glycol ether, and mixtures thereof. The alkanol can be selected from methanol, ethanol, n-propanol, isopropanol, butanol, pentanol, hexanol, their various positional isomers, and mixtures of the foregoing. In the invention, it has been found most preferable to use isopropanol, usually in conjunction with a glycol ether. It may also be possible to utilize in addition to, or in place of, said alkanols, the diols such as methylene, ethylene, propylene and butylene glycols, and mixtures thereof.

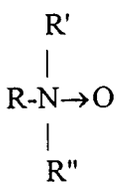
It is preferred to use an alkylene glycol ether solvent in this invention. The alkylene glycol ether solvents can include ethylene glycol monobutyl ether, ethylene glycol monopropyl ether, propylene glycol n-propyl ether, propylene glycol monobutyl ether, dipropylene glycol methyl ether, and mixtures thereof. Two preferred glycol ethers are ethylene glycol, monobutyl ether, also known as butoxyethanol, sold as butyl Cellosolve by Union Carbide, and propylene glycol n-propyl ether, available from a variety of sources.. Another preferred alkylene glycol ether is propylene glycol, t-butyl ether, which is commercially sold as Arcosolve PTB, by Arco Chemical Co. It has the structure:



Other suppliers of preferred solvents include Union Carbide. If mixtures of solvents are used. the amounts and ratios of such solvents used are important to determine the optimum cleaning and streak/film performances of the inventive cleaner. It is preferred to limit the total amount of solvent to no more than 50%, more preferably no more than 25%, and most preferably, no more than 15%, of the cleaner. A preferred range is about 1-15%.

The surfactant is selected from nonionic and amphoteric surfactants, and mixtures thereof.

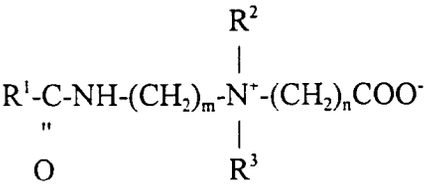
The nonionic surfactants are selected from alkoxylated alcohols, alkoxylated ether phenols, and other surfactants often referred to as semi-polar nonionics, such as the trialkyl amine oxides. The alkoxylated alcohols include ethoxylated, and ethoxylated and propoxylated C_{6-16} alcohols, with about 2-10 moles of ethylene oxide, or 1-10 and 1-10 moles of ethylene and propylene oxide per mole of alcohol, respectively. The semi-polar amine oxides are especially preferred, although, for the invention, a mixture of nonionic and amine oxide surfactants are most preferred. These have the general configuration:



wherein R is C_{6-24} alkyl, and R' and R" are both C_{1-4} alkyl, although R' and R" do not have to be equal. These amine oxides can also be ethoxylated or propoxylated. The preferred amine oxide is lauryl amine oxide, such as Barlox 12, from Lonza Chemical Company.

It has been surprisingly found that to obtain effective streaking/filming performance, the ratio of amine oxide:EDTA must be carefully controlled in the invention. The amount of amine oxide must exceed the amount of EDTA, more preferably exceeds 3:1 and most preferably is about 4:1 or greater.

The amphoteric surfactant is typically an alkylbetaine or a sulfobetaine. Especially preferred are alkylamidoalkyldialkylbetaines. These have the structure:



wherein R' is C_{6-20} alkyl, R^2 and R^3 are both C_{1-4} alkyl, although R^2 and R^3 do not have to be equal, and m can be 1-5, preferably 3, and n can be 1-5, preferably 1. These alkylbetaines can also be ethoxylated or propoxylated. The preferred alkylbetaine is a cocoamidopropyldimethyl betaine called Lonzaine CO, available from Lonza Chemical Co. Other vendors are Henkel KGaA, which provides Velvetex AB, and Sherex Chemical Co., which offers Varion CADG, both of which products are cocobetaines.

The amounts of surfactants present are to be somewhat minimized, for purposes of cost-savings and to generally restrict the dissolved actives which could contribute to leaving behind residues when the cleaner is applied to a surface. However, the amounts added are generally about 0.001-5%, more preferably 0.002-2.00% surfactant.

The invention further requires a cationic surfactant, specifically, a quaternary ammonium surfactant. These types of surfactants are typically used in bathroom cleaners because they are generally considered "broad spectrum" antimicrobial compounds, having efficacy against both gram positive (e.g., Staphylococcus sp.) and gram negative (e.g., Escherischia coli) microorganisms. However, it has been previously found that hard surface cleaners containing quaternary ammonium compounds typically leave residue and thus perform relatively poorly on glossy hard surfaces. Streaking/filming performance, as can be expected, is uniformly poor. However, because of the unique formulations of the invention in which the ratio of amine oxide to EDTA is carefully controlled, the inventive compositions have surprisingly superior streaking/filming performance compared to other quaternary ammonium-based cleaning formulations.

The builder is selected from the group consisting of: ethylene diamine tetraacetates (EDTA), alkali metal carbonates, alkali metal silicates, and mixtures thereof. Optionally, a co-builder selected from ammonium, alkali metal and alkaline earth metal hydroxides, may be desirable.

The builder is an important aspect of the invention. As mentioned above, there appears to be an interaction between the amine oxide surfactant and the builder, particularly EDTA. EDTA is known as a chelant, as well. The preferred builder is EDTA. Buffers, such as the above mentioned hydroxides, and such as ammonium carbamate, which has the structure $NH_2COO^-NH^+_4$, may also be desirable for inclusion. Other, potentially suitable buffers are guanidine derivatives, such as diaminoguanidine and guanidine carbonate; alkoxylalkylamines, such as isopropoxypropylamine, butoxypropylamine, ethoxypropylamine and methoxypropylamine; and alkylamines, such as ethyleneamine, ethylenediamine, ethylenetriamine, ethylenetetramine, diethylenetetramine, triethylenetetramine, tetraethylenepentamine, N,N-dimethylethylenediamine, N-methylenediamine, and other variations of the alkyl and amine substituents.

The amount of builder added should be in the range of 0.01-2%, more preferably 0.01-1%, by weight of the cleaner, while hydroxide, if present, should be added in the range of 0.001-1% by weight of the cleaner.

Since the cleaner is an aqueous cleaner with relatively low levels of actives, the principal ingredient is water, which should be present at a level of at least about 50%, more preferably at least about 80%, and most preferably, at least about 90%. Deionized water is most preferred.

Small amounts of adjuncts can be added for improving cleaning performance or aesthetic qualities of the cleaner. Adjuncts for cleaning include additional surfactants, such as those described in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Volume 22 pp. 332-432 (Marcel-Dekker. 1983), which are incorporated herein by reference. Aesthetic adjuncts include fragrances, such as those available from Givaudan, IFF, Quest and others, and dyes and pigments which can be solubilized or suspended in the formulation, such as diaminoanthraquinones. The amounts of these cleaning and aesthetic adjuncts should be in the range of 0-2%, more preferably 0-1%.

In the following Experimental section, the surprising performance benefits of the various aspects of the inventive cleaner are demonstrated.

EXPERIMENTAL

Two formulations, the first being inventive, the second being a comparative example, are set forth below as Examples 1-2.

Example 1

Ingredient	Wt. %
Quaternary ammonium surfactant[1]	0.6
NaOH	0.2
Nonionic surfactant[2]	0.25
Amine oxide surfactant[3]	2.2
Solvent[4]	3.0
Na_4EDTA[5]	0.56
D.I. H_2O	Q.S.[6]

[1] Barquat MB-50, C_{14} alkylbenzyldimethylammonium chloride (50% solution). In all of the following examples, if the same ingredient is listed and identified, the identification provided hereunder will be relied upon.

[2] Alfonic 610-50, C_{6-10} ethoxylated alcohol, about 3 moles of ethylene oxide per mole of alcohol (50% solution)

[3] Barlox 12, C_{12} alkyl dimethylamine oxide, from Lonza Inc., (30% solution)

[4] Ethylene glycol, monobutyl ether

[5] Builder, sodium ethylenediaminetetraacetate, 38% solution

[6] quantity sufficient to make up 100% formulation

Comparative Example 2

Ingredient	Wt. %
Quaternary ammonium surfactant	0.6
NaOH	0.2
Nonionic surfactant	0.25
Amine oxide surfactant	0.25
Solvent	2.0
Na_4EDTA	0.39
D.I. H_2O	Q.S.

[1] Unless further identified, all of the ingredients are the same as in the prior Example.

The two formulations 1 and 2 were compared against one another and against a number of commercially available cleaners for filming/streaking performance on glass mirror tiles. A grading scale of 0 to 10 was used, with 0 being worst and 10 being best. The results are tabulated below:

Table I

Filming/Streaking Performance

Example/Product	1	2	Lysol[1]	Formula 409®[2]
S/F Performance	7.7	2.3	3.9	8.3
Example/Product	Commercial Product 1	Commercial Product 2	Commercial Product 3	Commercial Product 4
S/F Performance	9.4	2.1	2	3.1

[1] L&F Products, Antibacterial Kitchen Cleaner, hard surface cleaner.

[2] The Clorox Company, hard surface cleaner.

As can be seen from the foregoing data, Example 1, which had the preferred >3:1 ratio of amine oxide: EDTA, clearly outperformed Example 2, as well as the commercial product Lysol Antibacterial Kitchen Cleaner, as well as commercial products 1-4, all of which are bactericidal products. Additionally, its streaking/filming performance was comparable to that of Formula 409® all purpose cleaner and commercial product 1, both of which are hard surface cleaners without bactericides.

Further examples of the invention are demonstrated in Examples 4-10 below:

Ingredient	Example 3	Example 4	Example 5	
NaOH	0.2%	0.2%	0.2%	
Quat.[1]	0.6%	0.6%	0.6%	
Nonionic[2]	0.25%	0.25%	0.25%	
Solvent[3]	2.0%	2.0%	2.0%	
EDTA	0.5%	1.5%	0.5%	
Amine Ox.[4]	2.0%	6.0%	4.0%	
D.I. H_2O	Q.S.	Q.S.	Q.S.	
Ingredient	**Example 6**	**Example 7**	**Example 8**	**Example 9**
NaOH	0.2%	0.2%	0.2%	0.2%
Quat.[1]	0.6%	0.6%	0.6%	0.4%
Nonionic[6]	0.25%	0.36%	0.36%	0.36%
Solvent[3]	2.0%	3.0%	2.0%	3.0%
EDTA	0.5%	0.5%	0.5%	0.5%
Amine Ox.[4]	2.0%	2.0%	2.0%	2.0%
D.I. H_2O	Q.S.	Q.S.	Q.S.	Q.S.

[1] Quaternary ammonium compound, Barquat MB-50

[2] Nonionic surfactant, Surfonic N-100, ethoxylated C_9alkylphenol, 10 moles of ethylene oxide, from Texaco Chemical.

[3] Ethylene glycol, monobutyl ether.

[4] C12 alkyl dimethylamine oxide (30%).

[5] Quantity sufficient to make up 100% solution.

[6] Nonionic surfactant, Alfonic 610-50.

Table II

Filming/Streaking Performance			
Example	3	4	5
S/F Performance	7.5	6.7	7.3
Example	6	7	
S/F Performance	7.9	7.7	

As can be seen from the above Table II, Inventive Examples 3-7, streaking/filming performance was excellent for these formulations. Examples 8-9, although ungraded by test panelists, were comparable to 3-7 by visual observation.

Further, in Table III below, the antimicrobial properties of certain of the inventive formulations were demonstrated. In these examples, ASTM Standard Test Method E1135-87 (1987), "Efficacy of Sanitizers Recommended for Inanimate Non-Food Contact Surfaces," (incorporated herein by reference thereto), was modified for use with the inventive formulations as the sanitzer solutions. As can be seen from the collected data, the inventive formulations possess excellent antimicrobial efficacy. Although not all formulations were tested, they would be expected to have similar efficacies.

Table III

Antimicrobial Efficacy after 1 Minute Contact with Formulations				
Bacterium	Example	1	5	6
Staph. aureus	% reduction	≧ 99.99%	≧ 99.99%	(not conducted)
Enterobacter aerogenes	% reduction	≧ 99.99%	(not conducted)	≧ 99.99%
	Example	7	9	
Staph. aureus	Example	≧ 99.99%	≧ 99.99%	
Klebsiella pneumoniae	Example	≧ 99.99%	≧ 99.99%	

Claims

1. An aqueous, antimicrobial hard surface cleaner with significantly improved residue removal and substantially reduced filming/streaking, said cleaner comprising:

   (a) an effective amount of a solvent selected from C_{1-6} alkanol, C_{3-24} alkylene glycol ether, and mixtures thereof;

   (b) an effective amount of a surfactant selected from amphoteric, nonionic surfactants, and mixtures thereof;

   (c) an effective amount of a quaternary ammonium surfactant;

   (d) an effective amount of a builder; and

   (d) the remainder as substantially all water.

2. The hard surface cleaner of claim 1 wherein said solvent is an alkylene glycol ether which is selected from the group consisting of ethylene glycol monobutyl ether, ethylene glycol monopropyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, and mixtures thereof.

3. The hard surface cleaner of claim 2 wherein said solvent is propylene glycol monobutyl ether.

4. The hard surface cleaner of claim 1 wherein said surfactant further comprises a mixture of nonionic and semi-polar nonionic surfactants.

5. The hard surface cleaner of claim 4 wherein said mixture comprises a mix of ethoxylated alcohol and amine oxide surfactants.

6. The hard surface cleaner of claim 5 wherein said builder is alkali metal ethylene diamine tetraacetate.

7. The hard surface cleaner of claim 6 wherein the ratio of amine oxide: alkali metal ethylene diamine tetraacetate is greater than 1:1.

8. The hard surface cleaner of claim 7 wherein the ratio of amine oxide: alkali metal ethylene diamine tetraacetate is greater than about 3:1.

9. A method of cleaning soil, without substantial residue remaining, from a hard surface comprising applying the cleaner of claim 1 to said soil and removing said soil and said cleaner.