



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 1/75, 7/08, 3/02, 3/20	A2	(11) International Publication Number: WO 95/07335 (43) International Publication Date: 16 March 1995 (16.03.95)
(21) International Application Number: PCT/US94/09240 (22) International Filing Date: 16 August 1994 (16.08.94) (30) Priority Data: 08/115,294 1 September 1993 (01.09.93) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor: WIERENGA, Thomas, James; 7981 Jasmine Trail, Cincinnati, OH 45241 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AU, BR, CA, FI, HU, JP, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: MILDLY ACIDIC HARD SURFACE CLEANING COMPOSITIONS CONTAINING AMINE OXIDE DETERGENT SURFACTANTS		
(57) Abstract Disclosed are mildly acidic liquid compositions for use in cleaning hard surfaces. The compositions contain from about 1 % to about 50 % of an amine oxide detergent surfactant, an aqueous carrier liquid, and an acidifying agent having a pK _a of less than about 6.0. The compositions contain enough of the acidifying agent to protonate at least about 10 % of the amine oxide species within the compositions and to provide a composition pH of between about 3 and 7. These no-rinse liquid hard surface cleaning compositions have excellent cleaning properties, they do not leave a visible residue when they dry, and they cause minimal or no staining of vinyl surfaces. Also disclosed are a method for cleaning vinyl surfaces using the liquid compositions, and non-liquid compositions from which the mildly acidic liquid compositions can easily be obtained by adding an aqueous liquid.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

MILDLY ACIDIC HARD SURFACE CLEANING COMPOSITIONS CONTAINING AMINE OXIDE DETERGENT SURFACTANTS

5

FIELD OF THE INVENTION

This invention relates to no-rinse hard surface cleaners which are mildly acidic and contain an amine oxide detergent surfactant. These compositions will effectively clean hard surfaces without leaving a visible residue when they dry and they will cause minimal or no staining of vinyl surfaces. The invention also relates to a process for cleaning vinyl surfaces using the compositions.

BACKGROUND OF THE INVENTION

The use of amine oxide detergent surfactants in cleaning compositions is well known. Amine oxides are most commonly used as cosurfactants to boost and maintain suds formation in laundry, shampoo, and dishwashing detergent compositions. Amine oxides have occasionally been used in hard surface cleaners such as acidic toilet bowl cleaners (pH of 2 or less), dishwashing liquids containing occlusive emollients (pH of 4 to 6.9), and selected non-acidic (neutral to alkaline) hard surface cleaners. In non-acidic hard surface cleaners, amine oxide detergent surfactants are essentially non-ionic (pK_a between about 4 and about 6). These nonionic amine oxides provide good cleaning properties and leave little or no visible residue on hard surfaces when they dry.

It was discovered, however, that non-acidic hard surface cleaners containing amine oxides will stain or discolor vinyl (polyvinyl chloride) surfaces. The staining amounts to a light yellow to dark brown discoloration of the vinyl. Staining will also occur on waxed vinyl surfaces where areas of wax are worn thin or are chipped away so that the amine oxide can come in direct contact with the vinyl.

It is therefore an object of the present invention to provide a hard surface cleaning composition containing amine oxide detergent surfactants that will cause minimal or no vinyl staining. It is a further object of the invention to provide such a composition which will also have superior cleaning properties and will not leave a visible residue on cleaned surfaces. It is also an object of this invention to provide a process for cleaning vinyl surfaces using such a composition.

35

SUMMARY OF THE INVENTION

In its product aspect, the present invention relates to mildly acidic, liquid hard

surface cleaning compositions comprising from about 1% to about 50% of an amine oxide detergent surfactant, an aqueous carrier liquid, and an acidifying agent having a pK_a of below about 6.0. The compositions contain the acidifying agent in an amount sufficient to establish a composition pH of between about 3 and 7 and in an amount sufficient to protonate at least about 10% of the amine oxide detergent surfactant in the composition. The present invention also embodies a non-liquid formulation from which the liquid composition can be derived. The non-liquid formulation is essentially the liquid composition wherein the amount of the aqueous carrier liquid is reduced (e.g., gel) or eliminated (e.g., granules).

10 In its method aspect, the present invention relates to a method for cleaning vinyl surfaces using the liquid compositions herein. In accordance with the method, the liquid compositions are applied in diluted or undiluted form to a vinyl surface. The diluted compositions have a pH of between about 3 and 7 and comprise from about 0.02% to about 0.2% of the amine oxide detergent surfactant, at least about 15 10% of which is protonated. The diluted or undiluted liquid compositions are applied to a vinyl surface, wiped with a porous material, and allowed to dry.

The liquid compositions can be used as no-rinse hard surface cleaners on floors, walls, etc. It was found that non-acidic liquid cleaning compositions containing amine oxides will stain vinyl surfaces. The liquid compositions of the present invention, however, will cause minimal or no vinyl staining. Moreover, the liquid compositions have excellent cleaning properties and will leave little or no visible residue when they dry.

BRIEF DESCRIPTION OF THE DRAWING

25 Figure 1 is a graph which shows the cleaning and residue profiles of several hard surface cleaners. The horizontal axis represents residue profiles based on a 0.0 (extremely visible residue) to 5.0 (no visible residue) scale. The vertical axis represents cleaning profiles (particulate soil removal) based on the percentage of soil removed via testing methods described hereinafter. Points A-E on the graph represent these profiles for commercially available hard surface cleaners. Point F 30 represents these profiles for a composition of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The liquid compositions of the present invention comprise three key elements:
35 1) an amine oxide detergent surfactant, 2) an acidifying agent, and 3) an aqueous carrier liquid. The liquid compositions can be used in diluted or undiluted form on hard surfaces.

As used herein, "mildly acidic" means a pH of between about 3.0 and 7.0. All pH values herein are measured in aqueous systems at 25°C (77°F).

As used herein, "vinyl" means material or surfaces containing polyvinyl chloride. Such material or surfaces can be waxed or unwaxed.

5 As used herein, "non-liquid" means granular, powder or gel formulations which can be diluted with the aqueous carrier liquid described hereinafter to produce a mildly acidic liquid hard surface cleaning composition of the present invention.

As used herein, "liquid compositions" mean the mildly acidic, liquid hard
10 surface cleaning compositions of the present invention, or aqueous dilutions thereof.

As used herein, all percentages and ratios are based on weight unless otherwise specified.

The present invention, in its product and process aspects, is described in
15 detail as follows.

Amine Oxide Detergent Surfactant

The compositions comprise an amine oxide detergent surfactant which typically has a pK_a of from about 4 to about 6. As described hereinafter, at least
20 about 10% of the amine oxide species within the composition must be in cationic (protonated) form.

Specifically, the compositions comprise from about 1% to about 50%, preferably from about 2% to about 30%, more preferably from about 2.5% to about 25%, of an amine oxide detergent surfactant. The amine oxide preferably has the
25 formula $RR'R''NO$, where R is a substituted or unsubstituted alkyl or alkene group containing from about 8 to about 30, preferably from about 8 to about 18, carbon atoms. Groups R' and R'' are each substituted or unsubstituted alkyl or alkene groups containing from about 1 to about 18, preferably from about 1 to about 4, carbon atoms. More preferably, R' and R'' are each methyl groups, examples of
30 which include dodecyldimethyl amine oxide, tetradecyldimethyl amine oxide, hexadecyldimethyl amine oxide, octadecyldimethyl amine oxide, and coconutalkyldimethyl amine oxides.

The amine oxide detergent surfactant can be prepared by known and conventional methods. One such method involves the oxidation of tertiary amines
35 in the manner set forth in U. S. Patent No. 3,223,647 and British Patent 437,566. In general terms, amine oxides are prepared by the controlled oxidation of the corresponding tertiary amines.

Examples of suitable amine oxide detergent surfactants for use in the compositions include dodecyldimethyl amine oxide, tridecyldimethyl amine oxide, tetradecyldimethyl amine oxide, pentadecyldimethyl amine oxide, hexadecyldimethyl amine oxide, heptadecyldimethyl amine oxide, octadecyldimethyl amine oxide, docetyl-diethyl amine oxide, tetradecyldimethyl amine oxide, hexadecyldiethyl amine oxide, octadecyldiethyl amine oxide, dodecyldipropyl amine oxide, tetradecyldipropyl amine oxide, hexadecyldipropyl amine oxide, octadecyldipropyl amine oxide, dodecyldibutyl amine oxide, tetradecyldibutyl amine oxide, hexadecyldibutyl amine oxide, octadecyldibutyl amine oxide, dodecylmethylethyl amine oxide, tetradecylethylpropyl amine oxide, hexadecylpropylbutyl amine oxide, and octadecylmethylbutyl amine oxide.

Also useful are the amine oxide detergent surfactants which are prepared by the oxidation of tertiary amines prepared from mixed alcohols obtainable from coconut oil. Such coconutalkyl amine oxides are preferred from an economic standpoint inasmuch as it is not necessary for the present purposes, to separate the mixed alcohol fractions into their pure components to secure the pure chain length fractions of the amine oxides.

Acidifying Agent

It was found that amine oxide staining of vinyl surfaces can be reduced or eliminated by using certain acidifying agents in the liquid composition. These acidifying agents are used to protonate a minimum percentage of amine oxide species in the liquid composition. It was also found that these protonated or cationic amine oxides species reduce (i.e., at 10% protonation) or eliminate (i.e., at 90-100% protonation) staining thus increasing the lifetime of the vinyl surface.

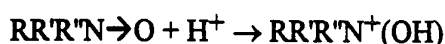
The composition herein comprises an acidifying agent having a pK_a of below about 6.0, preferably below about 5.0, more preferably below about 4.0. When selecting an acidifying agent, its pK_a should be less than that of the selected amine oxide, preferably from about 2 to about 3 units less, to provide for maximum protonation of the amine oxide species in the compositions.

The acidifying agent can contain organic acids, inorganic acids, or mixtures thereof. Preferred inorganic acids are H_2SO_4 , HCl, HNO_3 , H_3PO_4 , $HClO_3$ and mixtures thereof. Preferred organic acids are methane sulfonic acid, oxalic acid, glycerolphosphoric acid, ethylenediamine tetracetic acid (EDTA), diethylenetriamine pentaacetic acid (DTPA), maleic acid, mellitic acid, brucine tetrahydrate, benzenepentacarboxylic acid, pyromellitic acid, malonic acid, salicylic acid, hemimellitic acid, 1,4-piperazinebis-(ethanesulfonic) acid, tartaric acid,

fumaric acid, citric acid, o-phthalic acid, trimesic acid, dimethylmalonic acid, mandelic acid, malic acid, 1,1-cyclohexanediacetic acid, 2-methylpropane-1,2,3-tricarboxylic acid, hippuric acid, tricarballic acid, formic acid, 3,3-dimethylglutaric acid, 1,1-cyclopentanediacetic acid, itaconic acid, lactic acid, 5 barbituric acid, ascorbic acid, 2,2-dimethylsuccinic acid, succinic acid, benzoic acid, 2,2-dimethylglutaric acid, acetic acid, n-butyric acid and propionic acid. The acidifying agent is more preferably selected from the group of phosphoric acid, nitric acid, hydrochloric acid, oxalic acid, maleic acid, o-phthalic acid, and mixtures thereof. Most preferred are phosphoric acid, hydrochloric acid, nitric acid and 10 mixtures thereof.

The liquid compositions contain enough of the acidifying agent to establish a composition pH of between about 3.0 and 7.0, preferably between about 4.0 and about 6.0, more preferably between about 4.0 and about 5.5. Liquid amine oxide compositions employed on hard surfaces at a pH of less than 3.0 tend to harm 15 surface waxes, and when employed at a pH of 7.0 or above will cause excessive staining of vinyl surfaces.

The liquid compositions must also contain enough of the acidifying agent to protonate at least about 10% of the amine oxide species within the composition, preferably between about 50% and about 100%, more preferably between about 20 90% and 100%. As used herein, the term "protonated" refers to cationic amine oxide species containing a quaternary ammonium group. The protonation or conversion of nonionic to cationic amine oxides is represented generally by the reaction formula

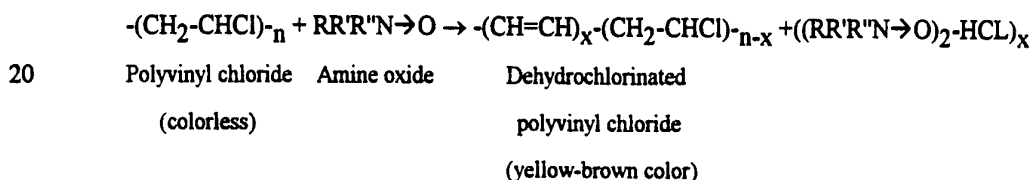


25 To achieve the requisite composition pH and amine oxide protonation, the concentration of the selected acid in the liquid compositions will typically be between about 0.005% and about 5%, more typically between about 0.005% and about 3% by weight of the liquid composition. Acid concentrations will vary depending on the pK_a of the amine oxide, the pK_a of the selected acidifying agent, 30 the desired target pH of the composition, and the chemical characteristics of other materials in the composition. Since the inorganic acids tend to have lower pK_a values than the organic acids, target pH values are more easily reached with the inorganic acids. Organic acids are less preferred in the composition because target pH values are more difficult to reach with higher pK_a acids and because they tend 35 to increase composition viscosity making them less desirable for handling and processing reasons. Inorganic acids can be combined with the weaker organic acids to more easily reach the target pH and to better control composition viscosity.

The liquid compositions can be used in diluted or undiluted form on hard surfaces. The compositions will typically be diluted with an aqueous liquid, usually tap water, prior to use. When diluted, the compositions comprise from about 0.02% to about 0.2%, preferably from about 0.04% to about 0.1%, of the amine oxide detergent surfactant. Whether diluted or undiluted, the liquid composition employed on hard surfaces must have the requisite composition pH and amine oxide protonation described herein.

The requisite pH of the composition is maintained by the amine oxide component. Amine oxide detergent surfactants normally have an adequate buffering capacity in the pH range described herein. Even when diluted with tap water, the amine oxide component can normally maintain the composition pH below 7.0. Additional buffers can be added if necessary to help maintain acidity. Such buffers are not usually necessary.

The vinyl staining described herein comes from the dehydrochlorination of polyvinyl chloride surfaces. It is believed that this dehydrochlorination reaction is accelerated by nonacidic amine oxide compositions. This accelerated dehydrochlorination is represented by the reaction formula



Dehydrochlorinated polyvinyl chloride has a yellow to brown appearance, depending on the degree of dehydrochlorination. This dehydrochlorination is believed to be accelerated by nonionic amine oxide species occasionally found in nonacidic liquid hard surface cleaners. By protonating the amine oxide to the extent described herein, and by maintaining an acidic environment, the rate of dehydrochlorination is greatly reduced and vinyl staining is reduced or eliminated. In the liquid compositions herein, the protonated amine oxides form ion pairs with the deprotonated acidifying agents. These ion pairs are much less reactive in dehydrochlorination reactions and do not penetrate vinyl surfaces as readily as nonionic amine oxide species.

The data summarized in Table 1 shows that mildly acidic, liquid amine oxide compositions of the present invention cause little or no staining when used on vinyl tiles.

Table 1
Dilute Product Vinyl Tile Staining From the Use
of Liquid Amine Oxide Compositions

Com- position	Coconut dimethyl amine oxide (gm/cc)	Acidifying agent	pK _a of acidifying agent	Concentration of acidifying agent (gm/cc)	Composition pH	Degree of vinyl staining
K	0.07	none	none	none	8.0	severe
L	0.07	H ₃ PO ₄	2.12	0.02	5.4	none
M	0.07	HCl	---	0.017	5.5	none
N	0.07	HNO ₃	---	0.017	5.4	none
O	0.07	H ₂ SO ₄	---	0.014	5.4	none
P	0.07	Maleic acid	2.00, 6.26	0.015	5.4	none
Q	0.07	Oxalic acid	1.19, 4.21	0.015	5.5	none
R	0.07	Ethylene diamine tetraacetic acid	1.7, 2.6, 6.3, 10.6	0.015	5.4	none
S	0.07	0-Phthalic acid	3.10, 5.27	0.015	5.4	light
T	0.07	Succinic acid	4.19, 5.57	0.015	5.4	light
U	0.07	Tartaric acid	3.02, 4.54	0.015	5.5	light
V	0.07	Citric acid	3.06, 4.74, 5.40	0.015	5.5	light
W	0.07	Malic acid	3.40, 5.05	0.013 / 0.051	5.4	light / moderate
X	0.07	Acetic acid	4.76	0.039	5.5	moderate

5

To generate the data summarized in Table 1, the following vinyl staining method was employed. This method accelerates staining but it correlates well with long term vinyl staining under normal conditions in the field. In accordance with this method, white vinyl floor tiles were rinsed with warm tap water, rinsed twice
10 with isopropanol, and then allowed to air dry. About 1cc of each composition K-X was separately applied to discreet regions of the tiles. The tiles were kept at room temperature for 1 hour and then placed in an oven at 60°C (140°F) for 1 hour, 45 minutes. The tiles were removed from the oven and allowed to cool to about room temperature. The cooled tiles were rinsed with tap water. The treated regions on
15 each tile were then visually inspected for vinyl staining. The degree of staining was rated as "none" (no color change), "light" (very slight but noticeable discoloration), "moderate" (yellow color change) or "severe" (brown color change). Each

composition K-X was a 1:128 dilution of a liquid concentrate with a pH of between about 4.0 and about 5.0. After dilution, each composition as applied to the tiles had a pH of between about 5.4 and 5.5. Each diluted composition therefore consisted of water, coconut dimethyl amine oxide, and a specific acidifying agent.

5 Composition K was the control product. It had a pH of about 8.0. Essentially 100% of the amine oxide surfactant was therefore in nonionic form. This composition caused severe staining.

 Compositions L-R were mildly acidic amine oxide compositions where 90-100% of the amine oxide species were protonated with acidifying agents having
10 pK_a values below about 3.0. Compositions L-R caused little or no vinyl staining.

 Compositions S-X contained weaker acids (pK_a values above about 3.0) which caused only light to moderate staining. Note however, that all of the mildly acidic compositions (L-X) caused significantly less staining than composition K which had a much higher pH (8.0) and therefore had less than 10% of its amine
15 oxide species in cationic form.

Aqueous Carrier Liquid

 The compositions herein are employed on hard surfaces in liquid form. Accordingly, the foregoing components are admixed with an aqueous carrier liquid.
20 The choice of aqueous carrier liquid is not critical. It must be safe and it must be chemically compatible with the components of the compositions. It should be either neutral or acidic to minimize the amount of acidifying agent needed.

 The aqueous carrier liquid can comprise solvents commonly used in hard surface cleaning compositions. Such solvents must be compatible with the
25 components of the compositions and must be chemically stable at the mildly acidic pH of the compositions. They should also have good filming/residue properties. Solvents for use in hard surface cleaners are described, for example, in U.S. Patent 5,108,660, which is incorporated herein by reference.

 Preferably, the aqueous carrier liquid is water or a miscible mixture of alcohol
30 and water. Water-alcohol mixtures are preferred inasmuch as the alcohol can aid in the dispersion and dissolution of the amine oxide and other materials in the compositions. Moreover, the alcohol can be used to adjust the viscosity of the compositions. The alcohols are preferably C₂-C₄ alcohols. Ethanol is most preferred.

35 Most preferably, the aqueous carrier liquid is water or a water-ethanol mixture containing from about 0% to about 50% ethanol.

Non-liquid Formulation

The present invention also embodies a non-liquid composition from which the mildly acidic, liquid hard surface cleaning compositions can easily be obtained by adding an aqueous carrier liquid. The non-liquid compositions can be in granular, powder or gel forms, preferably in granular forms.

The non-liquid compositions comprise from about 1% to about 50%, preferably from about 2% to about 30%, more preferably from about 2.5% to about 25%, of the amine oxide detergent surfactant described herein.

The non-liquid compositions also comprise an acidifying agent as described herein, preferably an organic acidifying agent. The non-liquid compositions contain enough of the acid to provide, upon dilution with the aqueous carrier liquid, a pH and percent amine oxide protonation within the ranges described herein for the mildly acidic, liquid compositions.

The non-liquid gel compositions contain reduced amounts of the non-aqueous carrier liquid. The non-liquid granular compositions contain substantially no aqueous carrier liquid. In either form, an aqueous carrier liquid is added to the non-liquid composition prior to use to form the mildly acidic, liquid hard surface cleaning compositions of the present invention.

Auxiliary Materials

Optionally, the compositions herein can contain auxiliary materials which augment cleaning and aesthetics.

The compositions can optionally comprise a non-interfering auxiliary surfactant in addition to the amine oxide detergent surfactant. Additional auxiliary surfactants can effect cleaning activity. A wide variety of organic, water soluble surfactants can optionally be employed. The choice of auxiliary surfactant depends on the desires of the user with regard to the intended purpose of the compositions and the commercial availability of the surfactant.

The compositions can contain any of the anionic, nonionic and zwitterionic / amphoteric surfactants commonly employed in liquid hard surface cleaning compositions.

Examples of compatible auxiliary surfactants useful in the compositions are set forth below. The term "alkyl" used to describe these various surfactants encompasses the hydrocarbyl alkyl groups having a chain length of from about C₈ to C₂₂, i.e., materials of the type generally recognized for use as detergents. Suitable surfactants which can be employed in the compositions herein include anionic surfactants such as the alkyl sulfates, alkyl benzene sulfonates, olefin

sulfonates, fatty acyl isethionates and taurides, alkyl sulfococates, alkyl ether sulfates (AE_2SO_4) and many others.

Examples of suitable nonionic surfactants include the polyethoxysorbitan esters, fatty acyl mono- and di-ethanol amides, C_8 - C_{22} ethoxylates and mixed
5 coconut ethoxylates containing 1 to 30 ethoxylate groups.

Examples of suitable zwitterionic surfactants include the fatty alkyl betaines and sulfobetaines and similar compounds such as C_8 to C_{18} ammonio propane sulfonate and C_8 to C_{18} hydroxy ammonio propane sulfonates.

The anionic surfactants can be in the form of their water soluble salts, for
10 instance the amine, ammonium, alkanolammonium or alkali metal salts. For most purposes it is preferred to use the anionic materials in their acid form to reduce the amount of auxiliary acid needed to acidify the composition. Especially preferred anionic surfactants herein the alkyl ether sulfates of the general formula AE_xSO_4 wherein $A=C_{10}$ - C'_{22} alkyl, E is ethylene oxide, and wherein x is an integer from 0
15 to 30; the C_{10} - C_{14} olefin sulfonates, and mixtures thereof.

Optionally, and preferably, the compositions contain water miscible substances having disinfectants properties. Preferred disinfectants are quaternary ammonium compounds, which are well known in the detergency art. Examples of suitable quaternary ammonium disinfectants include didecyl dimethyl ammonium
20 chloride, N-alkyl (C_{12} to C_{18}) dimethyl ammonium chloride, and N-alkyl (C_{12} to C_{18}) dimethyl ethyl benzyl ammonium chloride.

Other optional additives such as perfumes, brighteners, enzymes, colorants, and the like can be employed in the compositions to enhance aesthetics and/or cleaning performance. These additives must be acidic or neutral, they must be
25 compatible with the active components in the composition, and they should not interfere with the inhibition of vinyl staining provided by the compositions.

Detergent builders can also be employed in the compositions. These builders are especially useful when auxiliary surfactants or cosurfactants are employed, and are even more useful when the compositions are diluted prior to use with
30 exceptionally hard tap water., e.g., above about 12 grains. Detergent builders sequester calcium and magnesium hardness ions that might otherwise bind with and render less effective the auxiliary surfactants or cosurfactants. The detergent builders can be employed in the compositions at concentrations of between about 0% and about 10%.

35 Alkaline builder materials are not useful herein since they will interfere with the acidulation of the composition. Instead, the optional builder materials should comprise acidic or neutral sequestrants which do not interfere with the inhibition of

vinyl staining provided by the instant composition. Acidic or neutral builder materials include, for example, water soluble polycarboxylic acids (e.g., acrylic and maleic acid polymers and copolymers), polysulfonic acids, aminopolyacetic acids, and the like.

5 Suds suppressors are especially useful in the composition. In the hard surface cleaning composition herein, suds formation and maintenance are undesirably promoted by the amine oxide component. The compositions therefore preferably comprise a sufficient amount of a suds suppressor to prevent excessive sudsing during employment of the compositions on hard surfaces. Suds suppressors are
10 especially useful to allow for no-rinse application of the composition.

The suds suppressor can be provided by known and conventional means. Selection of the suds suppressor depends on its ability to formulate in the compositions, and the residue and cleaning profile of the compositions. The suds suppressor must be chemically compatible with the components in the
15 compositions, it must be functional at the pH range described herein, and it should not leave a visible residue on cleaned surfaces.

Low-foaming cosurfactants can be used as suds suppressor to mediate the suds profile in the compositions. Cosurfactant concentrations between about 1% and about 3% are normally sufficient. Examples of suitable cosurfactants for use
20 herein include block copolymers (e.g., Pluronic[®] and Tetronic[®], both available from BASF Company) and alkoxylated (e.g., ethoxylated/propoxylated) primary and secondary alcohols (e.g., Tergitol[®], available from Union Carbide; Poly-Tergent[®], available from Olin Corporation).

The optional suds suppressor preferably comprises a silicone-based material.
25 These materials are effective as suds suppressors at very low concentrations. The compositions preferably comprise from about 0.01% to about 0.50%, more preferably from about 0.01% to about 0.3%, of the silicone-based suds suppressor. At these low concentrations, the silicone-based suds suppressor is less likely to interfere with the cleaning performance of the compositions. Examples of suitable
30 silicone-based suds suppressors for use in the compositions include Dow Corning[®] AF-2210 and Dow Corning[®] AF-GPC, both available from Dow Corning Corporation.

These optional but preferred silicone-based suds suppressors can be incorporated into the composition by known and conventional means. Such
35 materials are typically water insoluble and require suspension in the aqueous environment of the compositions. The silicone-based suds suppressors are typically suspended by either increasing the viscosity of the liquid compositions or by

matching the specific gravity of the compositions with that of the silicone-based suds suppressor. The specific gravity of the compositions can be increased to that of the silicone-based suds suppressor, for example, by adding a low level of a cosurfactant. A preferred cosurfactant for this purpose are betaine zwitterionic surfactants, preferably at concentrations of from about 0.5% to about 3%.

Benefits

In addition to their effect on vinyl staining described hereinbefore, the compositions also have excellent cleaning properties and leave little or no visible residue on hard surfaces when they dry.

10 It was found that these compositions leave surprisingly little or no visible residue on hard surfaces whether used in a rinse or no-rinse application. As described hereinbefore, at least about 10% of the amine oxide species in the composition are cationic. Cationic surfactants, however, tend to form crystalline salts upon drying thus resulting in cloudy residues. This does not occur, however, 15 with the application (rinse or no-rinse application) of the instant compositions to hard surfaces.

It was also found that the compositions exhibit excellent particulate and greasy soil removal properties. This was surprising since acidic liquid hard surface cleaners do not typically clean particulate or greasy soil from hard surfaces as well 20 as non-acidic hard surface cleaners do. Acidic hard surface cleaners are used mostly in bathrooms to remove hard water stains.

The compositions provide excellent soil removal properties while also leaving little or no visible residue on cleaned surfaces. Hard surface cleaners typically have either good soil removal properties or good residue properties (e.g., they do not 25 leave a visible residue on cleaned surfaces), but not both. The compositions herein provide both of these desirable properties in a single product. It is therefor uniquely suited to clean, for example, heavily soiled shiny surfaces, e.g., waxed vinyl floors.

Figure 1 is a graph showing the relationship between particulate soil removal properties (vertical axis) and residue forming properties (horizontal axis) for the 30 several hard surface cleaning samples A-F listed below. These properties for samples A-F correspond to points A-F on the graph.

Sample A: Ecolab Oasis 266 All Purpose Cleaner 266

Labeled ingredients

5 nonyphenol ethoxylate
 n-alkyl (C₁₂₋₁₆) dimethyl benzyl ammonium chloride
 sodium ethylene diamine tetracetic acid
 water

Sample B: Scott #8 Neutral Floor Cleaner

Labeled ingredients

10 butoxyethanol
 alkylnaphthalene sodium sulfonate
 sodium citrate
 nonylphenol ethoxylate
 water

15

Sample C: S. C. Johnson G.P-Forward

Labeled ingredients

 sodium hydroxide
 sodium silicate
20 nonylphenol ethoxylate
 potassium hydroxide
 water

Sample D: S. C. Johnson Stride

25

Labeled ingredients

 C₁₂₋₁₈ ethoxylated/propoxylated alcohol
 citric acid
 sodium citrate
 water

30

Sample E: Butcher #4 Neutral Floor Cleaner

Labeled Ingredients

 isopropanol
 nonylphenol ethoxylate

35

Sample F: Example 1 composition

Ingredients

	coconut dimethyl amine oxide
	Betaine
5	Dow Corning® AF-2210
	Phosphoric acid
	Hydrochloric acid
	Dye/Perfume
	Deionized water (q.s. to 100%)
10	pH=4.0

Samples A-F are tested for residue formation on hard surfaces using the following method. Each sample is diluted to recommended usage with tap water (about 8 grain hardness) at between about 30° and about 38°C (between about 86° and about 100°F). About 5 grams of each diluted sample is applied to a folded lint-free towel wrapped around a small block, which is then used to apply the sample in one swipe lengthwise along a clean 3x12 inch chrome panel. After the applied sample dries, the residue remaining on the chrome panel is graded on an absolute scale of 0.0 (extremely visible residue) to 5.0 (no visible residue). The residue grade for each sample is then plotted along the horizontal axis of the graph in Figure 1.

Samples A-F are also tested for the ability to remove particulate soil from hard surfaces using the following method. White vinyl floor tiles are rinsed with warm tap water, rinsed twice with isopropanol, and allowed to dry. Particulate soil suspended in isopropanol (4.0 gram soil / 6.0 grams isopropanol / tile) is rubbed onto each tile with a lint-free paper towel. Once the isopropanol evaporates and the excess soil is brushed away, the tiles are washed with samples A-F using a Gardner Straight Line Washability Machine. Percentage of particulate soil removed by each sample is determined by reflectance measurements using Hunter Lab Tristimulus Colorimeter (DP-9000) before and after washing. Values representing the percentage of soil removed by each sample is then plotted along the vertical axis of the graph in Figure 1.

It can be seen in Figure 1 that Sample F, which is a composition of the present invention, is superior to samples A-E both in cleaning performance and in residue formation. This represents a significant departure from the trend seen in no-rinse hard surface cleaners that cleaning performance should decrease as residue formation tendencies decrease. Unlike most no-rinse hard surface cleaners, Sample

F exhibits excellent cleaning properties and residue/filming (i.e., leaves little or no visible film on cleaned surfaces) properties.

Method of Use

The present invention has been fully set forth in its composition aspects. The invention also encompasses a method for cleaning vinyl surfaces (waxed or unwaxed). The benefit of using this composition on vinyl surfaces is described hereinbefore.

The method comprises applying to a vinyl surface the mildly acidic liquid compositions herein or, preferably, applying an aqueous dilution thereof. The vinyl surface is then wiped with a porous material, e.g., cloth or mop, and allowed to dry.

In a preferred method, the mildly acidic liquid composition is first diluted with an aqueous liquid, preferably tap water. The diluted composition has a pH of between about 3.0 and 7.0, preferably between about 4.0 and about 6.0, and comprises from about 0.02% to about 0.2%, preferably from about 0.04% to about 0.1%, of the amine oxide detergent surfactant described herein. At least about 10% of the amine oxide species in the diluted composition are protonated, preferably from about 50% to about 100%, more preferably from about 90% to about 100%. The diluted composition is then applied to and wiped over (with a porous material) the vinyl surface and allowed to dry.

III. Examples

The following examples illustrate the compositions of the present invention, but are not intended to be limiting thereof.

25

Example 1

	Coconut dimethyl amine oxide	9.0%
	Betaine	1.0%
	Dow Corning® AF-2210	0.3%
30	Phosphoric acid	1.5%
	Hydrochloric acid	1.4%
	Dye/Perfume	0.8%
	Deionized water (q.s. to 100%)	pH = 4.0
	Amine oxide protonation	95-100%

35

Example 2

	Coconut dimethyl amine oxide	9.0%
	Dow Corning [®] AF-2210	0.3%
	Phosphoric acid	1.0%
5	Maleic acid	1.5%
	Dye/Perfume	0.8%
	Deionized water (q.s. to 100%)	pH = 4.0
	Amine oxide protonation	95-100%

10

Example 3

	Coconut dimethyl amine oxide	9.0%
	Dow Corning [®] AF-GPC	0.06%
	Nitric Acid	1.5%
	Dye/Perfume	0.8%
15	Deionized water (q.s. to 100%)	pH = 5.0
	Amine oxide protonation	75-85%

WHAT IS CLAIMED IS:

1. Mildly acidic, liquid hard surface cleaning compositions, comprising:
 - a) from 1% to 50% of an amine oxide detergent surfactant;
 - b) an aqueous carrier liquid; and
 - c) an acidifying agent having a pK_a of less than 6.0, preferably less than 4.0%;wherein
the pH of the liquid composition is between 3.0 and 7.0, preferably between 4.0 and 6.0, and at least 10% of the amine oxide detergent surfactant within the composition is protonated, preferably between 90% and 100% of the amine oxide detergent surfactant within the liquid composition is protonated.
2. A composition according to Claim 1 wherein the acidifying agent is selected from the group consisting of phosphoric acid, nitric acid, hydrochloric acid, oxalic acid, maleic acid, o-phthalic acid, and mixtures thereof, preferably the acidifying agent is selected from the group consisting of phosphoric acid, hydrochloric acid, nitric acid, and mixtures thereof.
3. A composition according to Claim 1 wherein the amine oxide detergent surfactant has the formula $RR'R''NO$, where R contains from 8 to 30 carbon atoms, and R' and R'' each contain from 1 to 18 carbon atoms, and said composition comprises from 2.5% to 25% of the amine oxide detergent surfactant.
4. A composition according to Claim 1 wherein said composition further comprises a suds suppressor and a quaternary disinfectant.
5. A method for cleaning vinyl surfaces, which method comprises the steps of:
 - a) obtaining a liquid composition which comprises:
 - i) from 1% to 50% of an amine oxide detergent surfactant;
 - ii) an aqueous carrier liquid; and
 - iii) an acidifying agent having a pK_a of less than 6.0, preferably less than 4.0,wherein the liquid composition has a pH of between 3 and 7, and at least 10% of the amine oxide detergent surfactant within the composition is protonated, preferably; between 90% and 100% of the amine oxide detergent surfactant is protonated
 - b) applying the liquid composition to a vinyl surface; and then

c) wiping the liquid composition over the vinyl surface with a porous material and allowing said vinyl surface to dry.

6. A method according to Claim 5 wherein the acidifying agent is selected from the group consisting of phosphoric acid, nitric acid, hydrochloric acid, oxalic acid, maleic acid, o-phthalic acid, and mixtures thereof, preferably the acidifying agent is selected from the group consisting of phosphoric acid, hydrochloric acid, nitric acid, and mixtures thereof.

7. A method according to Claim 5 wherein the amine oxide detergent surfactant has the formula $RR'R''NO$, where R contains from 8 to 18 carbon atoms, and R' and R'' each contain from 1 to 4 carbon atoms.

8. A method according to Claim 5 wherein the liquid composition further comprises a quaternary disinfectant and a suds suppressor.

9. A method according to Claim 5 further comprising the step of diluting the liquid composition in step 10(a) with an aqueous liquid wherein the diluted composition comprises from 0.02% to 0.2%, preferably from 0.04 to 0.1%, of the amine oxide detergent surfactant, and wherein the pH of the diluted composition is between 3 and 7 and at least 10% of the amine oxide detergent surfactant within the diluted composition is protonated.

10. Non-liquid hard surface cleaning compositions, comprising:

- a) from 1% to 50% of an amine oxide detergent surfactant; and
- b) an acidifying agent having a pK_a of less than 6.0; wherein
- c) said composition can be diluted with an aqueous carrier liquid to form a liquid composition having a pH between 3.0 and 7.0 and at least 10% of the amine oxide detergent surfactant within the liquid composition is protonated

1/1

