

Description**FIELD OF THE INVENTION**

5 This invention pertains to acidic liquid detergent compositions for bathrooms. Such compositions typically contain detergent surfactants, detergent builders, and/or solvents to accomplish their cleaning tasks.

BACKGROUND OF THE INVENTION

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The use of acidic cleaning compositions containing organic water-soluble synthetic detergents, solvents, and/or detergent builders for bathroom cleaning tasks are known. For example, DE-A-3 542 970 discloses detergent compositions comprising citric acid and/or dicarboxylic acids and as a thickening agent an alkylalcohol ether sulphate, an amphoteric surfactant, an amine oxide derivative or a particular amine or

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alkoxylated amine derivative. DE-A-3 542 970 does not disclose the hydrophobic solvents of the present invention which provide good cleaning functions. Indeed, the compositions known in the art are not usually capable of providing superior hard surface cleaning for all of the soils encountered in a bathroom.

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The object of the present invention is to provide detergent compositions which provide good cleaning for all of the usual hard surface cleaning tasks found in the bathroom including the removal of hard-to-remove soap scum and hard water deposits.

DETAILED DESCRIPTION OF THE INVENTION**(a) The Detergent Surfactants**

25 In accordance with the present invention, it has been found that mixtures of nonionic and zwitterionic detergent surfactants are required to provide superior cleaning on all of the soils found in a bathroom. The varied types of soils that may be encountered includes oily/greasy soils and soap scum. The combination of the two types of detergent surfactants provides good performance for all of the common types of soil encountered in the bathroom.

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Zwitterionic Detergent Surfactants

35 Zwitterionic detergent surfactants contain both cationic and anionic hydrophilic groups on the same molecule at a relatively wide range of pH's. The typical cationic group is a quaternary ammonium group, although other positively charged groups like sulfonium and phosphonium groups can also be used. The typical anionic hydrophilic groups are carboxylates and sulfonates, although other groups like sulfates, phosphates, etc. can be used. A generic formula for some preferred zwitterionic detergent surfactants is:

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wherein R is a hydrophobic group; R² and R³ are each C₁₋₄ alkyl, hydroxy alkyl or other substituted alkyl group which can also be joined to form ring structures with the N; R⁴ is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from one to four carbon atoms; and X is the hydrophilic group which is preferably a carboxylate or sulfonate group.

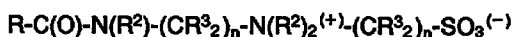
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Preferred hydrophobic groups R are alkyl groups containing from 8 to 22, preferably less than 18, more preferably less than 16, carbon atoms. The hydrophobic group can contain unsaturation and/or substituents and/or linking groups such as aryl groups, amido groups, ester groups, etc. In general, the simple alkyl groups are preferred for cost and stability reasons.

A specific "simple" zwitterionic detergent surfactant is 3-(N-dodecyl-N,N-dimethyl)-2-hydroxy-propane-1-sulfonate, available from the Sherex Company under the trade name "Varion HC".

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Other specific zwitterionic detergent surfactants have the generic formula:



wherein each R is a hydrocarbon, e.g., an alkyl group containing from 8 up to 20, preferably up to 18, more

preferably up to 16 carbon atoms, each (R^2) is either hydrogen or a short chain alkyl or substituted alkyl containing from one to about four carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, preferably methyl, each (R^3) is selected from the group consisting of hydrogen and hydroxy groups, and each n is a number from 1 to 4, preferably from 2 to 3; more preferably 3, with no more than one hydroxy group in any (CR^3_2) moiety. The R groups can be branched and/or unsaturated, and such structures can provide spotting/filming benefits, even when used as part of a mixture with straight chain alkyl R groups. The R^2 groups can also be connected to form ring structures. A detergent surfactant of this type is a C_{10-14} fatty acylamidopropylene-(hydroxypropylene)sulfobetaine that is available from the Sherex Company under the trade name "Varion CAS Sulfobetaine".

Compositions of this invention containing the above hydrocarbyl amido sulfobetaine (HASB) can contain more perfume and/or more hydrophobic perfumes than similar compositions containing conventional anionic detergent surfactants. This can be desirable in the preparation of consumer products. Perfumes useful in the compositions of this invention are disclosed in more detail hereinafter.

Other zwitterionic detergent surfactants useful herein include hydrocarbyl, e.g., fatty, amidoalkylenebetaines (hereinafter also referred to as "HAB"). These detergent surfactants have the generic formula:



wherein each R is a hydrocarbon, e.g., an alkyl group containing from 8 up to 20, preferably up to 18, more preferably up to 16 carbon atoms, each (R^2) is either hydrogen or a short chain alkyl or substituted alkyl containing from one to about four carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, preferably methyl, each (R^3) is selected from the group consisting of hydrogen and hydroxy groups, and each n is a number from 1 to 4, preferably from 2 to 3; more preferably 3, with no more than one hydroxy group in any (CR^3_2) moiety. The R groups can be branched and/or unsaturated, and such structures can provide spotting/filming benefits, even when used as part of a mixture with straight chain alkyl R groups.

An example of such a detergent surfactant is a C_{10-14} fatty acylamidopropylenebetaine available from the Miranol Company under the trade name "Mirataine BD".

The level of zwitterionic detergent surfactant in the composition is typically from about 0.01% to about 8%, preferably from about 1% to about 6%, more preferably from about 2% to about 4%. The level in the composition is dependent on the eventual level of dilution to make the wash solution. For cleaning, the composition, when used full strength, or the wash solution containing the composition, should contain from about 0.01% to about 8%, preferably from about 1% to about 6%, more preferably from about 2% to about 4%, of the zwitterionic detergent surfactant. Concentrated products will typically contain from about 0.02% to about 16%, preferably from about 4% to about 8% of the zwitterionic detergent surfactant.

Nonionic Detergent Cosurfactant

Compositions of this invention also contain nonionic detergent surfactant ("cosurfactant") to provide cleaning and emulsifying benefits over a wide range of soils. Nonionic cosurfactants useful herein include any of the well-known nonionic detergent surfactants that have an HLB of from about 6 to about 18, preferably from about 8 to about 16, more preferably from about 10 to about 14. Typical of these are alkoxylated (especially ethoxylated) alcohols and alkyl phenols, and the like, which are well-known from the detergency art. In general, such nonionic detergent surfactants contain an alkyl group in the C_8-22 , preferably C_{10-18} , more preferably C_{10-16} , range and generally contain from 2.5 to 12, preferably from 4 to 10, more preferably from 5 to 8, ethylene oxide groups, to give an HLB of from about 8 to about 16, preferably from about 10 to about 14. Ethoxylated alcohols are especially preferred in the compositions of the present type.

Specific examples of nonionic detergent surfactants useful herein include decyl polyethoxylate(2.5); coconut alkyl polyethoxylate(6.5); and decyl polyethoxylate(6).

A detailed listing of suitable nonionic surfactants, of the above types, for the detergent compositions herein can be found in U.S. Pat. No. 4,557,853, Collins, issued Dec. 10, 1985, incorporated by reference herein. Commercial sources of such surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1984, McCutcheon Division, MC Publishing Company, also incorporated herein by reference.

The nonionic cosurfactant component can comprise as little as 0.01% of the compositions herein, but typically the compositions will contain from about 0.1% to about 6%, more preferably from about 1% to about 4%, of nonionic cosurfactant.

The ratio of nonionic cosurfactant to zwitterionic detergent surfactant should be from about 1:4 to about 3:1, preferably from about 1:3 to about 2:1, more preferably from about 1:2 to about 1:1.

Optional Anionic Detergent Surfactant

Typical optional anionic detergent surfactants are the alkyl- and alkylethoxylate- (polyethoxylate) sulfates, paraffin sulfonates, olefin sulfonates, alpha-sulfonates of fatty acids and of fatty acid esters, and the like, which are well known from the detergency art. In general, such detergent surfactants contain an alkyl group in the C_9 - C_{22} , preferably C_{10} - C_{18} , more preferably C_{12} - C_{16} , range. The anionic detergent surfactants can be used in the form of their sodium, potassium or alkanolammonium, e.g., triethanolammonium salts. C_{12} - C_{18} paraffin-sulfonates and alkyl sulfates are especially preferred in the compositions of the present type.

A detailed listing of suitable anionic detergent surfactants, of the above types, for the detergent compositions herein can be found in U.S. Pat. No. 4,557,853, Collins, issued Dec. 10, 1985, incorporated by reference hereinbefore. Commercial sources of such surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1984, McCutcheon Division, MC Publishing Company, also incorporated hereinbefore by reference.

The optional anionic detergent cosurfactant component can comprise as little as 0.001% of the compositions herein when it is present, but typically the compositions will contain from about 0.01% to about 5%, more preferably from about 0.02% to about 2%, of anionic detergent cosurfactant, when it is present. Anionic detergent surfactants are desirably not present, or are present only in limited amounts to promote rinsing of the surfaces.

(b) The Hydrophobic Solvent

In order to obtain good cleaning, especially of lipid soils, it is necessary to use a hydrophobic solvent that has cleaning activity. The solvents employed in the hard surface cleaning compositions herein can be any of the well-known "degreasing" solvents commonly used in, for example, the dry cleaning industry, in the hard surface cleaner industry and the metalworking industry. The level of hydrophobic solvent is typically from about 1% to about 15%, preferably from about 2% to about 12%, most preferably from about 5% to about 10%.

Many of such solvents comprise hydrocarbon or halogenated hydrocarbon moieties of the alkyl or cycloalkyl type, and have a boiling point well above room temperature, i.e., above about 20°C.

The formulator of compositions of the present type will be guided in the selection of solvent partly by the need to provide good grease-cutting properties, and partly by aesthetic considerations. For example, kerosene hydrocarbons function quite well for grease cutting in the present compositions, but can be malodorous. Kerosene must be exceptionally clean before it can be used, even in commercial situations. For home use, where malodors would not be tolerated, the formulator would be more likely to select solvents which have a relatively pleasant odor, or odors which can be reasonably modified by perfuming.

The C_6 - C_9 alkyl aromatic solvents, especially the C_6 - C_9 alkyl benzenes, preferably octyl benzene, exhibit excellent grease removal properties and have a low, pleasant odor. Likewise, the olefin solvents having a boiling point of at least about 100°C, especially alpha-olefins, preferably 1-decene or 1-dodecene, are excellent grease removal solvents.

Generically, the glycol ethers useful herein have the formula $R^1 O(R^2 O)_m H$ wherein each R^1 is an alkyl group which contains from 4 to 8 carbon atoms, each R^2 is either ethylene or propylene, and m is a number from 1 to 3, and the compound has a solubility in water of less than about 20%, preferably less than about 10%, and more preferably less than about 6%. The most preferred glycol ethers are selected from the group consisting of dipropyleneglycolmonobutyl ether, monopropyleneglycolmonobutyl ether, diethyleneglycolmonohexyl ether, monoethyleneglycolmonohexyl ether, and mixtures thereof.

The butoxy-propanol solvent should have no more than about 20%, preferably no more than about 10%, more preferably no more than about 7%, of the secondary isomer in which the butoxy group is attached to the secondary atom of the propanol for improved odor.

A particularly preferred type of solvent for these hard surface cleaner compositions comprises diols having from 6 to 16 carbon atoms in their molecular structure. Preferred diol solvents have a solubility in water of from about 0.1 to about 20 g/100 g of water at 20°C.

Some examples of suitable diol solvents and their solubilities in water are shown in Table 1.

TABLE 1

Solubility of Selected Diols in 20 °C Water	
Diol	Solubility (g/100g H ₂ O)
1,4-Cyclohexanedimethanol	20.0*
2,5-Dimethyl-2,5-hexanediol	14.3
2-Phenyl-1,2-propanediol	12.0*
Phenyl-1,2-ethanediol	12.0*
2-Ethyl-1,3-hexanediol	4.2
2,2,4-Trimethyl-1,3-pentanediol	1.9
1,2-Octanediol	1.0*

*Determined via laboratory measurements.

All other values are from published literature.

The diol solvents are especially preferred because, in addition to good grease cutting ability, they impart to the compositions an enhanced ability to remove calcium soap soils from surfaces such as bathtub and shower stall walls. These soils are particularly difficult to remove, especially for compositions which do not contain an abrasive. The diols containing 8-12 carbon atoms are preferred. The most preferred diol solvent is 2,2,4-trimethyl-1,3-pentanediol.

Other solvents such as benzyl alcohol, n-hexanol, and phthalic acid esters of C₁₋₄ alcohols can also be used.

Terpene solvents and pine oil, are usable, but are preferably not present.

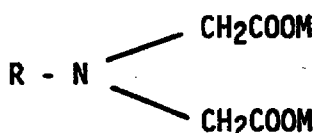
(c) The Polycarboxylate Detergent Builder

Polycarboxylate detergent builders useful herein, include the builders disclosed in U.S. Pat. No. 4,915,854, Mao et al., issued Apr. 10, 1990, said patent being incorporated herein by reference. Suitable detergent builders preferably have relatively strong binding constants for calcium under acid conditions. Preferred detergent builders include citric acid, and, especially, builders having the generic formula:



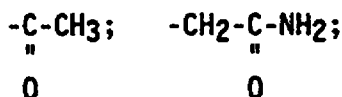
wherein each R⁵ is selected from the group consisting of H and OH and n is a number from about 2 to about 3 on the average. Other preferred detergent builders include those described in the copending U.S. Pat. Application Ser. No. 285,337 of Stephen Culshaw and Eddy Vos for "Hard-Surface Cleaning Compositions," filed Dec. 14, 1988, said patent application being incorporated herein by reference.

In addition to the above detergent builders, other detergent builders that are relatively efficient for hard surface cleaners and/or, preferably, have relatively reduced filming/streaking characteristics include the acid forms of those disclosed in U.S. Pat. No. 4,769,172, Siklosi, issued Sept. 6, 1988, and incorporated herein by reference. Still others include the chelating agents having the formula:



wherein R is selected from the group consisting of:

-CH₂CH₂CH₂OH; -CH₂CH(OH)CH₃; -CH₂CH(OH)CH₂OH; -CH(CH₂OH)₂; -CH₃; -CH₂CH₂OCH₃;



-CH₂CH₂CH₂OCH₃; -C(CH₂OH)₃; and mixtures thereof;
and each M is hydrogen.

Chemical names of the acid form of the chelating agents herein include:

N(3-hydroxypropyl)imino-N,N-diacetic acid (3-HPIDA);

5 N(2-hydroxypropyl)imino-N,N-diacetic acid (2-HPIDA);

N-glycerylimino-N,N-diacetic acid (GLIDA);

dihydroxyisopropylimino-(N,N)-diacetic acid (DHPIDA);

methylimino-(N,N)-diacetic acid (MIDA);

2-methoxyethylimino-(N,N)-diacetic acid (MEIDA);

10 amidiminodiacetic acid (also known as sodium amidonitrilotriacetic, SAND);

acetamidiminodiacetic acid (AIDA);

3-methoxypropylimino-N,N-diacetic acid (MEPIDA); and

tris(hydroxymethyl)methylimino-N,N-diacetic acid (TRIDA).

15 Methods of preparation of the iminodiacetic derivatives herein are disclosed in the following publications:

Japanese Laid Open publication 59-70652, for 3-HPIDA;

DE-OS-25 42 708, for 2-HPIDA and DHPIDA;

Chem. ZVESTI 34(1) p. 93-103 (1980), Mayer, Riećanska et al., publication of Mar. 26, 1979, for GLIDA;

C.A. 104(6)45062 d for MIDA; and

20 Biochemistry 5, p. 467 (1966) for AIDA.

The chelating agents of the invention are present at levels of from about 2% to about 14% of the total composition, preferably about 3% to about 12%, more preferably from about 5% to about 10%.

The acidic detergent builders herein will normally provide the desired pH in use. However, if necessary, the composition can also contain additional buffering materials to give a pH in use of from about 1 to about 25 5.5, preferably from about 2 to about 4.5, more preferably from about 3 to about 4.5. pH is usually measured on the product. The buffer is selected from the group consisting of: mineral acids such as HCl, HNO₃, etc. and organic acids such as acetic, succinic, tartaric, etc., and mixtures thereof. The buffering material in the system is important for spotting/filming. Preferably, the compositions are substantially, or completely free of materials like oxalic acid that are typically used to provide cleaning, but which are not 30 desirable from a safety standpoint in compositions that are to be used in the home, especially when very young children are present.

The Aqueous Solvent System

35 The balance of the formula is typically water. Nonaqueous polar solvents with only minimal cleaning action like methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, and mixtures thereof are usually not present. When the nonaqueous solvent is present, the level of nonaqueous polar solvent is from about 0.5% to about 10%, preferably less than about 5% and the level of water is from about 50% to about 97%, preferably from about 75% to about 95%.

Optional Ingredients

The compositions herein can also contain other various adjuncts which are known to the art for detergent compositions so long as they are not used at levels that cause unacceptable spotting/filming. 45 Nonlimiting examples of such adjuncts are:

Enzymes such as proteases;

Hydrotropes such as sodium toluene sulfonate, sodium cumene sulfonate and potassium xylene sulfonate; and

50 Aesthetic-enhancing ingredients such as colorants and perfumes, providing they do not adversely impact on spotting/filming in the cleaning of glass. The perfumes are preferably those that are more water-soluble and/or volatile to minimize spotting and filming.

Perfumes

55 Most hard surface cleaner products contain some perfume to provide an olfactory aesthetic benefit and to cover any "chemical" odor that the product may have. The main function of a small fraction of the highly volatile, low boiling (having low boiling points), perfume components in these perfumes is to improve the fragrance odor of the product itself, rather than impacting on the subsequent odor of the surface being

cleaned. However, some of the less volatile, high boiling perfume ingredients can provide a fresh and clean impression to the surfaces, and it is sometimes desirable that these ingredients be deposited and present on the dry surface. Perfume ingredients are readily solubilized in the compositions by the nonionic and zwitterionic detergent surfactants. Anionic detergent surfactants will not solubilize as much perfume, especially substantive perfume, or maintain uniformity to the same low temperature.

The perfume ingredients and compositions of this invention are the conventional ones known in the art. Selection of any perfume component, or amount of perfume, is based solely on aesthetic considerations. Suitable perfume compounds and compositions can be found in the art including U.S. Pat. Nos.: 4,145,184, Brain and Cummins, issued Mar. 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,515,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979, all of said patents being incorporated herein by reference.

In general, the degree of substantivity of a perfume is roughly proportional to the percentages of substantive perfume material used. Relatively substantive perfumes contain at least about 1%, preferably at least about 10%, substantive perfume materials.

Substantive perfume materials are those odorous compounds that deposit on surfaces via the cleaning process and are detectable by people with normal olfactory acuity. Such materials typically have vapor pressures lower than that of the average perfume material. Also, they typically have molecular weights of about 200 or above, and are detectable at levels below those of the average perfume material.

Perfume ingredients useful herein, along with their odor character, and their physical and chemical properties, such as boiling point and molecular weight, are given in "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969, incorporated herein by reference.

Examples of the highly volatile, low boiling, perfume ingredients are: anethole, benzaldehyde, benzyl acetate, benzyl alcohol, benzyl formate, iso-bornyl acetate, camphene, cis-citral (neral), citronellal, citronellol, citronellyl acetate, paracymene, decanal, dihydrolinalool, dihydromyrcenol, dimethyl phenyl carbinol, eucalyptol, geranial, geraniol, geranyl acetate, geranyl nitrile, cis-3-hexenyl acetate, hydroxycitronellal, d-limonene, linalool, linalool oxide, linalyl acetate, linalyl propionate, methyl anthranilate, alpha-methyl ionone, methyl nonyl acetaldehyde, methyl phenyl carbonyl acetate, laevo-menthyl acetate, menthone, iso-menthone, myrcene, myrcenyl acetate, myrcenol, nerol, neryl acetate, nonyl acetate, phenyl ethyl alcohol, alphapinene, beta-pinene, gamma-terpinene, alpha-terpineol, beta-terpineol, terpinyl acetate, and vertenex (para-tertiary-butyl cyclohexyl acetate). Some natural oils also contain large percentages of highly volatile perfume ingredients. For example, lavandin contains as major components: linalool; linalyl acetate; geraniol; and citronellol. Lemon oil and orange terpenes both contain about 95% of d-limonene.

Examples of moderately volatile perfume ingredients are: amyl cinnamic aldehyde, iso-amyl salicylate, beta-caryophyllene, cedrene, cinnamic alcohol, coumarin, dimethyl benzyl carbonyl acetate, ethyl vanillin, eugenol, iso-eugenol, flor acetate, heliotropine, 3-cis-hexenyl salicylate, hexyl salicylate, lillal (para-tertiarybutyl-alpha-methyl hydrocinnamic aldehyde), gamma-methyl ionone, nerolidol, patchouli alcohol, phenyl hexanol, betaselinene, trichloromethyl phenyl carbonyl acetate, triethyl citrate, vanillin, and veratraldehyde. Cedarwood terpenes are composed mainly of alpha-cedrene, beta-cedrene, and other C₁₅H₂₄ sesquiterpenes.

Examples of the less volatile, high boiling, perfume ingredients are: benzophenone, benzyl salicylate, ethylene brassylate, galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gama-2-benzopyran), hexyl cinnamic aldehyde, lyral (4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-10-carboxaldehyde), methyl cedrylone, methyl dihydro jasmonate, methyl-beta-naphthyl ketone, musk indanone, musk ketone, musk tibetene, and phenylethyl phenyl acetate.

Selection of any particular perfume ingredient is primarily dictated by aesthetic considerations, but more water-soluble materials are preferred, as stated hereinbefore, since such materials are less likely to adversely affect the good spotting/filming properties of the compositions.

These compositions have exceptionally good cleaning properties. They also have good "shine" properties, i.e., when used to clean glossy surfaces, without rinsing, they have much less tendency than e.g., phosphate built products to leave a dull finish on the surface.

In a preferred process for using the products described herein, and especially those formulated to be used at full strength, the product is sprayed onto the surface to be cleaned and then wiped off with a suitable material like cloth, a paper towel, etc. It is therefore highly desirable to package the product in a package that comprises a means for creating a spray, e.g., a pump, aerosol propellant and spray valve, etc.

All parts, percentages, and ratios herein are "by weight" unless otherwise stated.

The invention is illustrated by the following Examples.

EXAMPLE I

Ingredient	Weight %
3-(N-dodecyl-N,N-dimethyl)-2-hydroxy-propane-1-sulfonate (DDHPS)	2.0
Decyl polyethoxylate(2.5) (DPE2.5)	1.1
Decyl polyethoxylate(6.0) (DPE6)	2.9
Butoxy Propoxy Propanol (BPP)	5.0
Oxydisuccinic Acid (ODS)	10.0
Sodium Cumene Sulfonate (SCS)	4.2
Water, Buffering Agents, and Minors pH = 3.0	up to 100

EXAMPLE II

Ingredient	Weight %
DDHPS	2.0
DPE6	2.0
BPP	8.0
Citric Acid	10.0
SCS	1.6
Water, Buffering Agents, and Minors pH = 3.0	up to 100

EXAMPLE III

Ingredient	Weight %
DDHPS	2.0
DPE6	2.0
BPP	6.0
ODS	10.0
SCS	5.2
Water, buffering Agents, and Minors pH = 3.0	up to 100

EXAMPLE IV

A liquid hard surface cleaner composition is prepared according to the following formula:

Ingredient	Weight %
DDHPS	2.0
ODS	10.0
DPE6	2.0
BPP	6.0
SCS	7.5
Water, Buffering Agents, and Minors pH = 4.5	up to 100

EXAMPLE V

A composition is prepared according to the following formula:

Ingredient	Weight %
DDHPS	2.0
DPE6	2.0
Citric acid	10.0
BPP	6.0
SCS	8.9
Water, Buffering Agent, and Minors pH = 4.5	up to 100

EXAMPLE VI

Hard surface cleaning compositions are prepared according to the following formulae:

Composition A	
Ingredient	Weight %
DDHPS	6.0
DPE6	0.0
Citric Acid	10.0
BPP	5.0
Water, Buffering Agent, and Minors pH = 3.0	up to 100

Composition B	
Ingredient	Weight %
DDHPS	0.0
DPE6	6.0
Citric Acid	10.0
BPP	5.0
Water, Buffering Agent, and Minors pH = 3.0	up to 100

Composition C	
Ingredient	Weight %
DDHPS	4.0
DPE6	2.0
Citric Acid	10.0
BPP	5.0
Water, Buffering Agent, and Minors pH = 3.0	up to 100

When Compositions A, B, and C are tested on a soil that is representative of a shower wall, that contains a large amount of calcium soap, the percentage removal for A and B is 71% and the percentage removal for C is 85%. The combination of nonionic and zwitterionic detergent surfactants is clearly superior to the individual surfactants. The removal is comparable to that provided by a commercial product having a pH of about 1 that is more likely to cause damage to the surface being treated.

When the BPP solvent is replaced by a less hydrophobic solvent, the removal of more oily soils is much less. For example, when the BPP is replaced by the more common butyl cellosolve, the removal of a typical oily soil found in the bathroom is reduced by about one fourth. The combination of the nonionic and

zwitterionic detergent surfactants; the detergent builder that is effective at low pH; and the hydrophobic solvent provides a hard surface cleaner that is effective on the typical soap scum encountered in the bathroom and also on other more oily soils that can be encountered in the bathroom.

5 EXAMPLE VII

	Ingredient	Weight %
10	3-(N-cetyl-N,N-dimethyl)propane-1-sulfonate	2.0
	DPE2.5	1.1
	DPE6	2.9
	ODS	10.0
	BPP	5.0
15	Water, Buffering Agents, and Minors pH = 2.5	up to 100

This composition provides satisfactory removal of the shower wall soil of Example VI.

20 Claims

1. An acidic aqueous hard surface detergent composition comprising: (a) mixture of zwitterionic detergent surfactant, preferably wherein said zwitterionic detergent surfactant has the formula:



wherein R is a hydrophobic group; R² and R³ are each C₁₋₄ alkyl, hydroxy alkyl or other substituted alkyl group which can also be joined to form ring structures with the N; R⁴ is a moiety joining the cationic nitrogen atom to the hydrophilic group and is an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 4 carbon atoms; and X is the hydrophilic group which is a carboxylate or sulfonate group, and nonionic detergent surfactant, preferably having an Hydrophylic Lipophylic balance (HLB) of from about 10 to about 14; (b) hydrophobic solvent that provides a cleaning function, in an amount of from about 1% to about 15%, and said solvent having a solubility in water of less than about 20%; (c) polycarboxylate detergent builder; and (d) the balance being an aqueous solvent system and optional minor ingredients, the pH of said composition being from about 1 to about 5.5, preferably from about 2 to about 4.5.

2. The composition of Claim 1 wherein said solvent (b) is selected from the group consisting of alkyl and cycloalkyl hydrocarbons and halohydrocarbons, alpha olefins, benzyl alcohol, glycol ethers, and diols containing 6 to 16 carbon atoms, preferably either a diol containing from 8 to 12 carbon atoms, or 2,2,4-trimethyl-1,3-pentanediol.

3. The composition of Claim 2 wherein said solvent (b) has the formula R¹O(R²O)_mH wherein each R¹ is an alkyl group which contains from 4 to 8 carbon atoms, each R² is selected from the group consisting of ethylene or propylene, and m is a number from 1 to 3, preferably a solvent selected from the group consisting of dipropyleneglycolmonobutyl ether, monopropyleneglycolmonobutyl ether, diethyleneglycolmonohexyl ether, monoethyleneglycolmonohexyl ether, and mixtures thereof.

4. The composition of any of Claims 1-3 wherein said zwitterionic detergent surfactant is a hydrocarbyl-amidoalkylenesulfobetaine having the formula:



wherein each R is an alkyl group containing from 8 to 20 carbon atoms, each (R²) is selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, each (R³) is selected from the group consisting of hydrogen and hydroxy groups, and each n is a number from 1 to 4; with no more than one hydroxy group in any (CR³)₂ moiety.



zwitterionic detergent surfactants; the detergent builder that is effective at low pH; and the hydrophobic solvent provides a hard surface cleaner that is effective on the typical soap scum encountered in the bathroom and also on other more oily soils that can be encountered in the bathroom.

5 EXAMPLE VII

	Ingredient	Weight %
10	3-(N-cetyl-N,N-dimethyl)propane-1-sulfonate	2.0
	DPE2.5	1.1
	DPE6	2.9
	ODS	10.0
	BPP	5.0
15	Water, Buffering Agents, and Minors pH = 2.5	up to 100

This composition provides satisfactory removal of the shower wall soil of Example VI.

20 Claims

1. An acidic aqueous hard surface detergent composition comprising: (a) mixture of zwitterionic detergent surfactant, preferably wherein said zwitterionic detergent surfactant has the formula:



wherein R is a hydrophobic group; R² and R³ are each C₁₋₄ alkyl, hydroxy alkyl or other substituted alkyl group which can also be joined to form ring structures with the N; R⁴ is a moiety joining the cationic nitrogen atom to the hydrophilic group and is an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 4 carbon atoms; and X is the hydrophilic group which is a carboxylate or sulfonate group, and nonionic detergent surfactant, preferably having an Hydrophilic Lipophylic balance (HLB) of from about 10 to about 14; (b) hydrophobic solvent that provides a cleaning function, in an amount of from about 1% to about 15%, and said solvent having a solubility in water of less than about 20%; (c) polycarboxylate detergent builder; and (d) the balance being an aqueous solvent system and optional minor ingredients, the pH of said composition being from about 1 to about 5.5, preferably from about 2 to about 4.5.

2. The composition of Claim 1 wherein said solvent (b) is selected from the group consisting of alkyl and cycloalkyl hydrocarbons and halohydrocarbons, alpha olefins, benzyl alcohol, glycol ethers, and diols containing 6 to 16 carbon atoms, preferably either a diol containing from 8 to 12 carbon atoms, or 2,2,4-trimethyl-1,3-pentanediol.

3. The composition of Claim 2 wherein said solvent (b) has the formula R¹O(R²O)_mH wherein each R¹ is an alkyl group which contains from 4 to 8 carbon atoms, each R² is selected from the group consisting of ethylene or propylene, and m is a number from 1 to 3, preferably a solvent selected from the group consisting of dipropyleneglycolmonobutyl ether, monopropyleneglycolmonobutyl ether, diethyleneglycolmonohexyl ether, monoethyleneglycolmonohexyl ether, and mixtures thereof.

4. The composition of any of Claims 1-3 wherein said zwitterionic detergent surfactant is a hydrocarbyl-amidoalkylenesulfobetaine having the formula:



wherein each R is an alkyl group containing from 8 to 20 carbon atoms, each (R²) is selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, each (R³) is selected from the group consisting of hydrogen and hydroxy groups, and each n is a number from 1 to 4; with no more than one hydroxy group in any (CR³)₂ moiety.

5. The composition of any of Claims 1-4 wherein the level of said zwitterionic detergent surfactant is from about 0.01% to about 8%; the level of said nonionic detergent surfactant is from about 0.1% to about 6%; the ratio of said nonionic to said zwitterionic detergent surfactant is from about 1:4 to about 3:1; the level of said hydrophobic solvent is from about 1% to about 15%; the level of said polycarboxylate detergent builder is from about 2% to about 14%; and the pH of said composition is from about 2 to about 4.5.
6. The composition of Claim 5 wherein the level of said zwitterionic detergent surfactant is from about 1% to about 6%; the level of said nonionic detergent surfactant is from about 0.5% to about 6%; the ratio of said nonionic to said zwitterionic detergent surfactant is from about 1:3 to about 2:1; the level of said hydrophobic solvent is from about 2% to about 12%; the level of said polycarboxylate detergent builder is from about 3% to about 12%; and the pH of said composition is from about 2 to about 4.5.
7. The process of cleaning hard surfaces comprising spraying said surfaces with any of the compositions of Claims 1-6.

Patentansprüche

1. Saure wäßrige Detergensenzusammensetzung für harte Oberflächen, umfassend: (a) ein Gemisch aus einem zwitterionischen grenzflächenaktiven Detergensmittel, worin das genannte zwitterionische grenzflächenaktive Detergensmittel vorzugsweise die Formel:

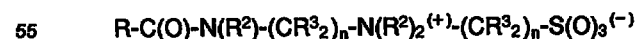


- besitzt, worin R eine hydrophobe Gruppe darstellt; R² und R³ jeweils eine C₁₋₄-Alkyl-, -hydroxyalkyl- oder eine andere substituierte Alkylgruppe sind, welche auch verbunden sein können, um mit dem Stickstoffatom Ringstrukturen auszubilden; R⁴ ein Rest ist, welcher das kationische Stickstoffatom an die hydrophile Gruppe bindet und für eine Alkyl-, Hydroxyalkyl- oder Polyalkoxygruppe mit 1 bis 4 Kohlenstoffatomen steht; und X die hydrophile Gruppe darstellt, welche eine Carboxylat- oder Sulfonatgruppe ist, und einem nichtionischen grenzflächenaktiven Detergensmittel, welches vorzugsweise ein Hydrophil-Lipophil-Gleichgewicht (HLB) von etwa 10 bis etwa 14 aufweist;
- (b) ein hydrophobes Lösungsmittel, welches eine Reinigungsfunktion gewährleistet, vorzugsweise in einer Menge von etwa 1% bis etwa 15%, und welches Lösungsmittel eine Löslichkeit in Wasser von weniger als etwa 20% besitzt;
- (c) einen Polycarboxylatdetergensgerüststoff; und
- (d) als Rest ein wäßriges Lösungsmittelsystem und fakultative geringfügige Bestandteile, wobei der pH-Wert der genannten Zusammensetzung von etwa 1 bis etwa 5,5, vorzugsweise von etwa 2 bis etwa 4,5 beträgt.

2. Zusammensetzung nach Anspruch 1, worin das genannte Lösungsmittel (b) von der aus Alkyl- und Cycloalkylkohlenwasserstoffen und Halogenkohlenwasserstoffen, alpha-Olefinen, Benzylalkohol, Glykolethern und Diolen mit 6 bis 16 Kohlenstoffatomen bestehenden Gruppe ausgewählt ist, vorzugsweise entweder ein Diol mit 8 bis 12 Kohlenstoffatomen oder 2,2,4-Trimethyl-1,3-pentandiol ist.

3. Zusammensetzung nach Anspruch 2, worin das genannte Lösungsmittel (b) die Formel R¹O(R²O)_m-H besitzt, worin jeder Rest R¹ eine Alkylgruppe darstellt, welche 4 bis 8 Kohlenstoffatome besitzt, jeder Rest R² von der aus Ethylen oder Propylen bestehenden Gruppe ausgewählt ist und m eine Zahl von 1 bis 3 bedeutet, vorzugsweise ein Lösungsmittel ist, welches von der aus Dipropylenglykolmonobutylether, Monopropylenglykolmonobutylether, Diethylenglykolmonohexylether, Monoethylenglykolmonohexylether und Gemischen hievon bestehenden Gruppe ausgewählt ist.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, worin das genannte zwitterionische grenzflächenaktive Detergensmittel ein Hydrocarbyl-amidoalkylensulfobetain der Formel



ist, worin jeder Rest R eine Alkylgruppe mit 8 bis 20 Kohlenstoffatomen darstellt, jeder Rest (R²) von der aus Methyl, Ethyl, Propyl, Hydroxy-substituiertem Ethyl oder Propyl und Gemischen hievon

bestehenden Gruppe ausgewählt ist, jeder Rest (R^3) von der aus Wasserstoff und Hydroxygruppen bestehenden Gruppe ausgewählt ist und jedes n eine Zahl von 1 bis 4 darstellt; mit nicht mehr als einer Hydroxygruppe in jedem beliebigen (CR^3_2)-Rest.

- 5 5. Zusammensetzung nach einem der Ansprüche 1 bis 4, worin die Menge an dem genannten zwitterionischen grenzflächenaktiven Detergensmittel von etwa 0,01% bis etwa 8% beträgt; die Menge an dem genannten nichtionischen grenzflächenaktiven Detergensmittel von etwa 0,1% bis etwa 6% beträgt; das Verhältnis von dem genannten nichtionischen grenzflächenaktiven Detergensmittel zu dem genannten zwitterionischen grenzflächenaktiven Detergensmittel von etwa 1:4 bis etwa 3:1 beträgt; die Menge an dem genannten hydrophoben Lösungsmittel von etwa 1% bis etwa 15% beträgt; die Menge an dem genannten Polycarboxylatdetergensgerüststoff von etwa 2% bis etwa 14% beträgt; und der pH-Wert der genannten Zusammensetzung von etwa 2 bis etwa 4,5 ist.
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- 15 6. Zusammensetzung nach Anspruch 5, worin die Menge an dem genannten zwitterionischen grenzflächenaktiven Detergensmittel von etwa 1% bis etwa 6% beträgt; die Menge an dem genannten nichtionischen grenzflächenaktiven Detergensmittel von etwa 0,55 bis etwa 6% beträgt; das Verhältnis von dem genannten nichtionischen grenzflächenaktiven Detergensmittel zu dem genannten zwitterionischen grenzflächenaktiven Detergensmittel von etwa 1:3 bis etwa 2:1 beträgt; die Menge an dem genannten hydrophoben Lösungsmittel von etwa 2% bis etwa 12% beträgt; die Menge an dem genannten Polycarboxylatdetergensgerüststoff von etwa 3% bis etwa 12% beträgt; und der pH-Wert der genannten Zusammensetzung von etwa 2 bis etwa 4,5 ist.
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- 25 7. Verfahren zur Reinigung von harten Oberflächen, umfassend das Besprühen der genannten Oberflächen mit irgendeiner der Zusammensetzungen nach den Ansprüchen 1 bis 6.

Revendications

- 30 1. Composition détergente acide aqueuse pour surfaces dures comprenant : (a) un mélange d'un agent tensio-actif détergent zwitterionique, de préférence dans lequel ledit agent tensio-actif détergent zwitterionique a pour formule :



35 dans lequel R est un groupe hydrophobe; R^2 et R^3 sont chacun un groupe alkyle en C_1 - C_4 , hydroxyalkyle ou un autre groupe alkyle substitué qui peut également être joint pour former des structures cycliques avec l'atome de N; R^4 est un radical joignant l'atome d'azote cationique au groupe hydrophile et est un groupe alkylène, hydroxyalkylène ou polyalcoxy contenant 1 à 4 atomes de carbone; et X est le groupe hydrophile qui est un groupe carboxylate ou sulfonate, et d'un agent tensioactif détergent non ionique, de préférence ayant un rapport hydrophile/lipophile (HLB) d'environ 10 à environ 14; (b) un solvant hydrophobe qui assure une fonction de nettoyage, de préférence en quantité d'environ 1 à environ 15 %, ledit solvant ayant une solubilité dans l'eau inférieure à environ 20 %; (c) un adjuvant de détergent polycarboxylate; et (d) le restant étant un système solvant aqueux et des ingrédients mineurs facultatifs, le pH de ladite composition étant d'environ 1 à environ 5,5, de préférence d'environ 2 à environ 4,5.

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- 50 2. Composition selon la revendication 1, dans laquelle ledit solvant (b) est sélectionné dans le groupe formé des hydrocarbures et halogénohydrocarbures alkyliques et cycloalkyliques, des alpha-oléfinés, de l'alcool benzylique, des glycol-éthers et des diols contenant 6 à 16 atomes de carbone, de préférence un diol contenant 8 à 12 atomes de carbone ou le 2,2,4-triméthyl-1,3-pentanediol.
- 55 3. Composition selon la revendication 2, dans laquelle ledit solvant (b) a pour formule $R^1O(R^2O)_mH$ dans laquelle R^1 est un groupe alkyle qui contient 4 à 8 atomes de carbone, chaque R^2 est sélectionné dans le groupe formé par l'éthylène et le propylène, et m est un nombre de 1 à 3, de préférence un solvant choisi dans le groupe formé du dipropylèneglycolmonobutyl éther, du monopropylèneglycolmonobutyl-éther, du diéthylèneglycolmonohexyl-éther, du monoéthylèneglycolmonohexyl-éther et de leurs mélanges.

4. Composition selon l'une quelconque des revendications 1 à 3, dans laquelle ledit agent tensioactif détergent zwitterionique est une amidoalkylènesulfobétaïne d'hydrocarbyle ayant pour formule :



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dans laquelle chaque R est un groupe alkyle contenant 8 à 20 atomes de carbone, chaque (R²) est choisi dans le groupe formé des groupes méthyle, éthyle, propyle, éthyle ou propyle hydroxy-substitué et leurs mélanges, chaque (R³) est choisi dans le groupe formé de l'hydrogène et des groupes hydroxy, et chaque n est un nombre de 1 à 4 ; pas plus d'un groupe hydroxy n'étant présent dans un radical (CR³) quelconque.

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5. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle le niveau dudit agent tensio-actif détergent zwitterionique est d'environ 0,01 % à environ 8 % ; le niveau dudit agent tensio-actif détergent non ionique est d'environ 0,1 % à environ 6 % ; le rapport dudit agent tensio-actif détergent non ionique audit agent tensio-actif détergent zwitterionique est d'environ 1:4 à environ 3:1; le niveau dudit solvant hydrophobe est d'environ 1 % à environ 15 %; le niveau dudit adjuvant de détergence polycarboxylate est d'environ 2 % à environ 14 %; et le pH de ladite composition est d'environ 2 à environ 4,5.

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6. Composition selon la revendication 5, dans laquelle le niveau dudit agent tensio-actif détergent zwitterionique est d'environ 1 % à environ 6 % ; le niveau dudit agent tensio-actif détergent non ionique est d'environ 0,5 % à environ 6 %, le rapport dudit agent tensio-actif détergent non ionique audit agent tensioactif détergent zwitterionique est d'environ 1:3 à environ 2:1; le niveau dudit solvant hydrophobe est d'environ 2 % à environ 12 %; le niveau dudit adjuvant de détergence polycarboxylate est d'environ 3 % à environ 12 %; et le pH de ladite composition est d'environ 2 à environ 4,5.

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7. Procédé de nettoyage de surfaces dures consistant à pulvériser sur lesdites surfaces l'une quelconque des compositions des revendications 1 à 6.

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