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(54) Acidic cleaning compositions

(57) The present invention is a liquid acidic composition comprising an acid, and a surfactant system comprising from 0.01% to 10% by weight of the total composition of an amine oxide according to the formula R1R2R3NO, wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and from 0.01% to 10% by weight of the total composition of an amine according to the formula RR'R"N, wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms, or hydrogen. Said compositions deliver excellent limescale removal performance as well as outstanding greasy soap scum cleaning on hard-surfaces.

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Description

Technical field

The present invention relates to cleaning compositions for hard-surfaces. More specifically, the compositions of the present invention give optimal performance in removing limescale-containing stains typically found in a kitchen or in a bathroom.

Background

Tap water contains a certain amount of solubilized ions which upon water evaporation eventually deposit as salts such as calcium carbonate on surfaces which are often in contact with said water, resulting in an unaesthetic aspect of said surfaces. This limescale formation and deposition phenomenon is even more acute in places where water is particularly hard.

It is well-known in the art that limescale deposits can be chemically removed with acidic solutions, and a great variety of acidic cleaning compositions have been described for this purpose.

However, the state of the art liquid acidic limescale removal compositions do not perform equally well on all limescale-containing stains, particularly on limescale-containing stains which can be found in bathrooms or in kitchens, i.e., on stains containing mineral deposits like calcium and/or magnesium carbonate but also high amount of organic deposits such as greasy soap scum. Indeed, the presence of such greasy soap scum is detrimental to the limescale removal performance of acidic compositions.

Thus, liquid acidic limescale removal compositions have been formulated that comprise on top of the acid, a surfactant to deliver effective cleaning on organic soils. Representative of the art is for example, EP-A-496 188 which discloses acidic compositions comprising maleic acid and nonionic surfactants for the cleaning of limescale-containing bathroom-type stains.

However, it has now been observed that surfactants like nonionic surfactants have a negative impact on limescale removal properties of acids, and thus decrease the limescale removal performance of an acidic composition comprising them. Also such compositions based on acids and nonionic surfactants are not fully satisfactory from a consumer point of view in terms of greasy soap scum cleaning.

There is a constant strive for the development of limescale removal compositions with better performance in several respects including improved greasy soap scum cleaning performance and excellent limescale removal performance.

It is therefore an object of the present invention to provide a liquid composition for the removal of limescale-containing stains which can be found in a kitchen or in a bathroom, said composition delivering improved greasy soap scum cleaning while exhibiting also excellent limescale removal performance.

It has now been found that the above object is met by formulating an acidic liquid composition comprising an acid and a particular surfactant system, namely an amine oxide according to the formula R1R2R3NO, wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and an amine according to the formula RR'R"N, wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms or hydrogen. Indeed, it has been found that the compositions of the present invention comprising an acid, e.g., maleic acid alone or together with a second acid, and said surfactant system provides significantly improved greasy soap scum cleaning performance as well as improved limescale removal performance, as compared to the same compositions but with another surfactant, for example a nonionic surfactant, instead of said surfactant system, this even at a lower total surfactant level.

In a broader aspect the present invention also encompasses the use of an amine, as described herein, and/or of an amine oxide, as described herein, in an acidic liquid composition, to improve the greasy soap scum cleaning performance of said composition.

EP-A-601 990 discloses an acidic composition comprising an acid for example maleic acid together with a thickening system comprising from 0.5% to 15% by weight of the total composition of a mixture of a nonionic surfactant and a cationic surfactant. No amine oxides or amines are disclosed.

WO 95/07335 discloses mildly acidic (pH=3 to 7) no-rinse hard surfaces liquid compositions. The compositions contain from 1% to 50% by weight of an amine oxide and an acidifying agent having a pKa of less than 6. No primary, secondary or tertiary amines are disclosed.

GB 1 240 469 discloses a hard-surface cleaning composition which has a pH of not more than 7 and comprises (a) an inorganic or organic acid, or an acidic salts (5% to 95%), (b) a cationic surfactant (0.01% to 10%), and (c) a covalent compound other than (b) and which contains oxygen or a halogen and at least one hydrocarbon chain having at least four carbon atoms. The cationic surfactants disclosed are C8-24 amine oxides. No tertiary, secondary or primary amines are disclosed.

EP-A-130 786 discloses an acidic composition (pH=1 to 5) comprising a weak organic and a weak inorganic acid (5% to 25%), a surfactant system comprising a major proportion of an amine oxide (2% to 15%) and a cosolvent, said composition being preferably applied to the soils as a foam. Sulphamic acid is mentioned amongst the weak inorganic acids. No primary, secondary or tertiary amines are disclosed.

GB 2 106 927 discloses liquid thickened toilet bowl cleaners comprising a non volatile water soluble organic acid, a surfactant (e.g., amine oxide), and a cellulose ether, said composition having a pH of 2.2 to 3.5. No primary, secondary or tertiary amines are disclosed.

EP-A-253 676 discloses a thickened aqueous composition comprising at least one acidic salt, e.g., maleic acid (0.01%-30%), and a thickening agent (0.1% to 10%) which is at least one of the compounds selected from the group consisting of amine or amine oxide surfactants. No mixture of amine and amine oxide surfactants is expressly described, nor exemplified. EP-A-253 676 does not refer to the removal of limescale-containing stains like those found in bathrooms or in kitchens.

Summary of the invention

The present invention is a liquid acidic composition comprising an acid, and a surfactant system comprising from 0.01% to 10% by weight of the total composition of an amine oxide according to the formula R1R2R3NO, wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and from 0.01% to 10% by weight of the total composition of an amine according to the formula RR'R"N, wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms, or hydrogen.

The present invention also encompasses a process of treating hard-surfaces soiled by limescale-containing stains wherein an acidic liquid composition according to the present invention is applied in its neat form or in diluted form, onto said surfaces, then left to act onto said surfaces and then removed by rinsing.

The present invention further encompasses the use, of a surfactant system comprising an amine oxide according to the formula R1R2R3NO, wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and/or an amine according to the formula RR'R"N, wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms, or hydrogen, in an acidic limescale removal composition, to improve the greasy soap scum cleaning performance of said composition.

Detailed description of the invention

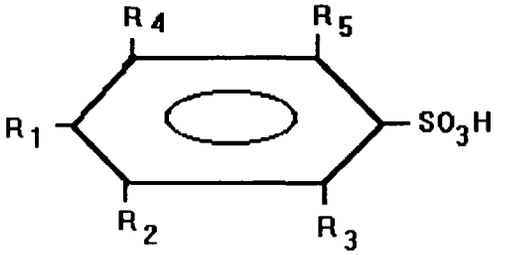
The compositions according to the present invention are designed for removing limescale deposits. Thus, they comprise as a first essential ingredient an acid. Typically, the acids to be used herein may be any inorganic or organic acid well-known to those skilled in the art, or mixtures thereof. Said compositions may comprise up to 80 % by weight of the total composition of said acid, or mixtures thereof.

Preferred herein the compositions of the present invention comprise maleic acid. Accordingly, the compositions according to the present invention comprise from 0.1% to 45% by weight of the total composition of maleic acid, preferably from 1% to 25% and more preferably from 8% to 20%. This percentage is calculated on the basis of the molecular weight of the acid form, but maleic anhydride is equally convenient for use in the compositions according to the present invention. Indeed maleic anhydride is generally cheaper and it is transformed into the acid form when incorporated in an aqueous medium. In one embodiment of the present invention maleic acid is used alone as the acid of the acidic compositions of the present invention.

In another embodiment of the present invention, a second acid is added on top of said maleic acid. Said second acid is desired to strengthen the limescale removal performance. Preferably the second acids to be used herein which are particularly efficient to remove limescale on many surfaces, have their first pKa not exceeding 5, more preferably not exceeding 3, and most preferably not exceeding 2. According to the present invention said acids can be organic or inorganic acids. Examples of inorganic acids are sulphonic acid derivatives, sulphamic acid (pKa=0.1), hydrochloric acid (pKa<0), nitric acid (pKa<0), phosphoric acid (pKa=2.1) and sulphuric acid (pKa=0.4). An example of organic acid is citric acid (pKa=3.06). Particularly suitable to be used herein are sulphonic acid derivatives including alkyl sulphonic acids and aryl sulphonic acids.

Suitable alkyl sulphonic acids for use herein are C1-C6 linear or branched alkylsulphonic acids or mixtures thereof, such as methanesulphonic acid (pKa=1.9) commercially available for example from Aldrich, William Blythe & Co. Ltd. or Elf. Atochem.

Suitable aryl sulphonic acids for use herein are according to the formula :



wherein R_1, R_2, R_3, R_4 and R_5 are each H or SO_3H, or linear or branched C_1-C_4 alkyl chain; or mixtures thereof.

Preferred arylsulphonic acids to be used according to the present invention are those which comprise no or only one alkyl chain. Indeed, we have found that said arylsulphonic acids are particularly effective at removing limescale, which is not the case for their longer alkyl chain homologues. Also, we have found that said arylsulphonic acids are particularly safe to the surface treated therewith. Particularly suitable arylsulphonic acids for use herein are benzene sulphonic acid (pKa=0.7), toluene sulphonic acid and cumene sulphonic acid. Amongst these three, at equal weight %, we have found that the shorter the alkyl chain, down to no chain at all, the better the limescale removing performance.

Preferred acids having a first pKa not exceeding 5 to be used herein are sulphamic acid, sulphuric acid, aryl sulphonic acids, alkyl sulphonic acids, or mixtures thereof, more preferred are sulphamic acid, sulphuric acid, benzene sulphonic acid or mixtures thereof and highly preferred is sulphamic acid.

The compositions of the present invention comprise from 0.1% to 25% by weight of the total composition of a second acid which has a first pKa not exceeding 5, or mixtures thereof, preferably from 0.1% to 20%, more preferably from 0.1% to 10% and most preferably from 0.1% to 7%.

The compositions according to the present invention comprise as a second essential ingredient a surfactant system comprising an amine oxide, as described hereinafter, and an amine, as described hereinafter.

Suitable amine oxides to be used herein are according to the following formula $R_1R_2R_3NO$ wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms, and preferably of from 1 to 20 carbon atoms. Particularly preferred amine oxides to be used according to the present invention are amine oxides having the following formula $R_1R_2R_3NO$ wherein R1 is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of 1 to 30 carbon atoms, preferably of 8 to 20 carbon atoms, more preferably of 6 to 16, most preferably of 8 to 14, and wherein R2 and R3 are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups, or mixtures thereof.

Suitable amine oxides for use herein are for instance coconut dimethyl amine oxides, C12-C16 dimethyl amine oxides. Said amine oxides may be commercially available from Hoechst, Stephan, AKZO (under the trade name Aromox®) or FINA (under the trade name Radiamox®).

The compositions of the present invention comprise from 0.01% to 10% by weight of the total composition of said amine oxide, or mixtures thereof, preferably from 0.1% to 5% and more preferably from 0.1% to 3%.

Suitable amines to be used herein are according to the following formula RR'R"N wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms, and preferably of from 1 to 20 carbon atoms and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms or hydrogen. Particularly preferred amines to be used according to the present invention are amines having the following formula RR'R"N wherein R is a saturated or unsaturated, linear or branched alkyl group of 1 to 30 carbon atoms, preferably of 8 to 20 carbon atoms, more preferably of 6 to 16, most preferably of 8 to 14 and wherein R' and R" are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups, or mixtures thereof.

Suitable amines for use herein are for instance C12 dimethyl amine, coconut dimethyl amine, C12-C16 dimethyl amine. Said amines may be commercially available from Hoechst under the trade name Genamin®, AKZO under the trade name Aromox® or Fina under the trade name Radiamox®.

The compositions of the present invention comprise from 0.01% to 10% by weight of the total composition of said amine, or mixtures thereof, preferably from 0.1% to 5% and more preferably from 0.1% to 3%.

The preferred liquid acidic compositions herein comprise said amine and said amine oxide in a weight ratio of said amine to said amine oxide of 10:1 to 1:10, preferably of 5:1 to 1:5 and most preferably of 1:1 to deliver optimum physical stability and optimum greasy soap scum cleaning.

It has been found that the incorporation of an amine, as defined herein, in the preferred liquid acidic compositions

of the present invention which comprise maleic acid alone or together with a second acid, as described herein, and said amine oxide, allows to formulate liquid acidic compositions with improved physical stability. Indeed, the addition of an amine, as described herein, to a liquid acidic composition comprising maleic acid and an amine oxide, as described herein, provides improved physical stability to said composition, as compared to the physical stability of the same composition without said amine. Actually, in absence of amines, amine oxides tend to precipitate when added in a liquid acidic composition comprising maleic acid. It is speculated that the addition of amines to a liquid acidic composition comprising maleic acid and an amine oxide, as described therein, reduces the formation of amine oxide - maleic acid salts, reducing thereby the precipitation effect. It is further speculated that amines also improve the solubility of said amine oxide -maleic acid salts that may have formed, thereby further preventing the precipitation effect.

The surfactant system according to the present invention allows to lower the surface tension and to improve the wettability of the surfaces being cleaned with the liquid acidic compositions of the present invention. The presence of said surfactant system in the liquid acidic compositions of the present invention helps to solubilize the soils and to improve the streaking profile of the acids.

It has now been found that the addition, in an acidic liquid composition, of the surfactant system according to the present invention, i.e., an amine oxide, as described herein, and an amine, as described herein, provides improved greasy soap scum cleaning performance as well as improved limescale removal performance, as compared to the greasy soap scum cleaning performance and limescale removal performance obtained with the same composition but with another surfactant like a nonionic surfactant, e.g. an alcohol ethoxylate (Dobanol® 91-8), instead of said surfactant system, this even at significantly lower total surfactant level.

In a broader aspect of the present invention, it has been found that the addition of an amine, as defined herein, and/or of an amine oxide, as defined herein, in a liquid acidic composition provides improved greasy soap scum cleaning performance, as compared to the same composition without any surfactant, or to the same composition but with another surfactant, e.g. a nonionic surfactant, this while providing excellent limescale removal performance. Thus, the present invention also encompasses the use, in an acidic liquid limescale removal composition, of a surfactant system comprising an amine, as defined herein, and/or an amine oxide, as defined herein, to improve the greasy soap scum cleaning performance of said composition.

The liquid compositions according to the present invention are preferably aqueous. Accordingly, the compositions according to the present invention comprise from 10% to 95% by weight of the total composition of water, preferably from 50% to 90%, most preferably from 70% to 85%.

The compositions according to the present invention are liquid acidic compositions. Accordingly, the compositions according to the present invention have a pH as is below 3, preferably in the range of from 0.1 to 2.5, more preferably of from 0.1 to 2, and most preferably of from 0.3 to 1.5.

The acidic liquid compositions of the present invention are physically stable, i.e. that no phase separation occurs when stored in rapid aging test (RAT) at 50 °C for 10 days or at 2 °C for 2 months.

The compositions according to the present invention may further comprise a variety of other ingredients including other surfactants, colorants, bactericides, thickeners, dyes, chelants, pigments, solvents, stabilizers, perfumes, corrosion inhibitors and the like.

Accordingly the compositions according to the present invention may further comprise other surfactants or mixtures thereof. The compositions according to the present invention may comprise up to 30% by weight of the total composition of said other surfactant or mixtures thereof on top of the surfactant system of the present invention, more preferably from 0.05% to 10%, more preferably from 0.1% to 8%, and most preferably from 0.1% to 3%. All types of surfactants may be used in the present invention including nonionic, anionic, cationic, amphoteric or zwitterionic surfactants. It is also possible to use mixtures of such surfactants without departing from the spirit of the present invention.

Suitable nonionic surfactants to be used herein are alkoxylated alcohol nonionic surfactants which can be readily made by condensation processes which are well-known in the art. However, a great variety of such alkoxylated alcohols, especially ethoxylated and/or propoxylated alcohols is also conveniently commercially available. Surfactants catalogs are available which list a number of surfactants, including nonionics.

Accordingly, preferred alkoxylated alcohols for use herein are nonionic surfactants according to the formula RO(E)e(P)pH where R is a hydrocarbon chain of from 2 to 24 carbon atoms, E is ethylene oxide and P is propylene oxide, and e and p which represent the average degree of, respectively ethoxylation and propoxylation, are of from 0 to 24. The hydrophobic moiety of the nonionic compound can be a primary or secondary, straight or branched alcohol having from 8 to 24 carbon atoms. Preferred nonionic surfactants for use in the compositions according to the invention are the condensation products of ethylene oxide with alcohols having a straight alkyl chain, having from 6 to 22 carbon atoms, wherein the degree of ethoxylation is from 1 to 15, preferably from 5 to 12. Such suitable nonionic surfactants are commercially available from Shell, for instance, under the trade name Dobanol® or from Shell under the trade name Lutensol®. These nonionics are preferred because they have been found to allow the formulation of a stable product without requiring the addition of stabilisers or hydrotopes. When using other nonionics, it may be necessary to add hydrotopes such as cumene sulphonate or solvents such as butyldiglycolether.

Suitable anionic surfactants for use herein are according to the formula R_1SO_3M wherein R_1 represents a hydro-

carbon group selected from the group consisting of straight or branched alkyl radicals containing from 6 to 24 carbon atoms and alkyl phenyl radicals containing from 6 to 15 carbon atoms in the alkyl group. M is a salt forming cation which typically is selected from the group consisting of sodium, potassium, ammonium, and mixtures thereof.

Other suitable anionic surfactants can be represented by the water-soluble salts of an alkyl sulfate or an alkyl polyethoxylate ether sulfate wherein the alkyl group contains from 6 to 24 carbon atoms, and preferably from 1 to 30 ethoxy groups for the alkyl polyethoxylate ether sulfates.

Suitable cationic surfactants to be used herein include derivatives of quaternary ammonium, phosphonium, imidazolium and sulfonium compounds. Preferred cationic surfactants for use herein are according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion, R_1 is a C_8-C_{20} hydrocarbon chain and R_2, R_3 and R_4 are independently selected from H or C_1-C_4 hydrocarbon chains. In a preferred embodiment of the present invention, R_1 is a C_{10}-C_{18} hydrocarbon chain, most preferably C_{12}, C_{14}, or C_{16}, and R_2, R_3 and R_4 are all three methyl, and X is halogen, preferably bromide or chloride, most preferably bromide. Examples of cationic surfactants are lauryl trimethyl ammonium bromide, stearyl trimethyl ammonium bromide (STAB), cetyl trimethyl ammonium bromide (CTAB) and myristyl trimethyl ammonium bromide (MTAB). Highly preferred herein are lauryl trimethyl ammonium salts.

Indeed, it has been found that the addition of a cationic surfactant according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion, R_1 is a C_8-C_{12} hydrocarbon chain and R_2, R_3 and R_4 are independently selected from H or C_1-C_4 hydrocarbon chains, and preferably of lauryl trimethyl ammonium salts, in a liquid acidic composition, allows to improve the limescale removal performance of said composition. Thus, another aspect of the present invention is the use of a cationic surfactant according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion, R_1 is a C_8-C_{12} hydrocarbon chain and R_2, R_3 and R_4 are independently selected from H or C_1-C_4 hydrocarbon chains, preferably of lauryl trimethyl ammonium salts, in a liquid acidic composition, to improve the limescale removal performance of said composition.

Suitable zwitterionic 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 phosphonium, imidazolium and sulfonium groups can be used. The typical anionic hydrophilic groups are carboxylates and sulfonates, although other groups like sulfates, phosphonates, and the like can be used. A generic formula for some preferred zwitterionic surfactants is

$$R_1\text{-}N^+(R_2)(R_3)R_4X^-$$

wherein R_1 is a hydrophobic group; R_2 and R_3 are each C_1-C_4 alkyl, hydroxy alkyl or other substituted alkyl group which can also be joined to form ring structures with the N; R_4 is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 4 carbon atoms; and X is the hydrophilic group which is preferably a carboxylate or sulfonate group. Preferred hydrophobic groups R_1 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 and the like. In general, the simple alkyl groups are preferred for cost and stability reasons.

Other specific zwitterionic surfactants have the generic formulas:

$$R_1\text{-}C(O)\text{-}N(R_2)\text{-}(C(R_3)_2)_n\text{-}N(R_2)_2{}^{(+)}\text{-}(C(R_3)_2)_n\text{-}SO_3{}^{(-)} \text{ or } R_1\text{-}C(O)\text{-}N(R_2)\text{-}(C(R_3)_2)_n\text{-}N(R_2)_2{}^{(+)}\text{-}(C(R_3)_2)_n\text{-}COO^{(-)}$$

wherein each R_1 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 a hydrogen (when attached to the amido nitrogen), short chain alkyl or substituted alkyl containing from one to 4 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 $(C(R_3)_2)$ moiety. The R_1 groups can be branched and/or unsaturated. The R_2 groups can also be connected to form ring structures. A surfactant of this type is a C_{10}-C_{14} fatty acylamidopropylene(hydroxypropylene)sulfobetaine that is available from the Sherex Company under the trade name "Varion CAS sulfobetaine"®.

Suitable amphoteric surfactants are surfactants which are similar to the zwitterionic surfactants but without the quaternary group. However, they contain an amine group that is protonated at the low pH of the composition to form cationic group and they may also possess an anionic group at these pHs.

The compositions according to the present invention are particularly suitable for treating hard-surfaces soiled by limescale-containing stains. By "limescale-containing stains" it is meant herein any pure limescale stains, i.e., any stains composed essentially of mineral deposits as well as limescale-containing stains typically found, for example, in a kitchen or in a bathroom, i.e., stains which contain not only mineral deposits like calcium and/or magnesium carbonate but also soap scum (e.g., calcium stearate) and grease. Actually, the compositions of the present invention exhibit excellent limescale removing performance when used to treat any types of surfaces soiled by limescale-containing

stains comprising not only pure limescale deposits but also at least 10% by weight of the total stain of organic deposits like soap scum and grease, preferably more than 30%. Such surfaces can be found in bathrooms, kitchens, but also in appliances including large appliances such as automatic dish washers and/or washing machines.

Accordingly, the present invention encompasses a process of treating hard-surfaces soiled by limescale-containing stains wherein an aqueous acidic liquid composition according to the present invention is applied in its neat form or in diluted form, onto said surfaces, then left to act onto said surfaces and then removed by rinsing.

The expression "used in diluted form" herein includes dilution by the user. Typical dilution levels are of from 0.5% to 50% by weight of the composition.

The expression "treating" includes removing limescale deposits while being safe to the surfaces treated as well as cleaning greasy soap scum stains due to the presence of said surfactant system.

Examples

The present invention is further illustrated by the following examples. These compositions were made comprising the listed ingredients in the listed proportions (weight %).

Ingredients: (% by weight)	Compositions					
	I	II	III	IV	V	VI
Maleic acid	10	--	7	2	10	8
Sulphamic acid	2	10	1	4	--	--
Citric acid	--	--	--	--	2	--
C12 dimethyl amine	0.5	--	--	0.8	--	--
Coconut dimethyl amine	--	0.4	--	--	1	--
C12-C16 dimethyl amine	--	--	0.5	--	--	--
Coconut dimethyl amine oxide	0.5	0.4	--	--	0.5	1
C12-C16 dimethyl amine oxide	--	--	0.5	0.4	--	--
C8 dimethyl amine	--	--	--	--	--	1
LTAB*	--	--	0.5	--	--	0.4
Waters & Minors	----------up to 100 ----------					

LTAB* stands for lauryl trimethyl ammonium bromide.

All the compositions of the above examples exhibit excellent limescale removal performance as well as outstanding greasy soap scum cleaning performance when used to clean limescale-containing stains found in a kitchen and in a bathroom, this both when used neat or in diluted form.

Claims

1. A liquid acidic composition comprising an acid, and a surfactant system comprising from 0.01% to 10% by weight of the total composition of an amine oxide according to the formula R1R2R3NO, wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and from 0.01% to 10% by weight of the total composition of an amine according to the formula RR'R"N, wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms or hydrogen.

2. A composition according to claim 1 wherein said acid is an organic or inorganic acid or a mixture thereof at a level up to 80% by weight of the total composition.

3. A composition according to any of the preceding claims wherein said acid is maleic acid alone or together with a second acid which has its first pKa not exceeding 5, or mixtures thereof.

4. A composition according to claim 3 wherein said second acid is sulphamic acid, alkylsulfonic acid, arylsulfonic acid, citric acid, nitric acid, sulphuric acid, phosphoric acid, hydrochloric acid or mixtures thereof.

5. A composition according to claims 3 or 4 wherein said composition comprises from 0.1% to 45% by weight of the total composition of maleic acid, preferably from 1% to 25%, and more preferably from 8% to 20%, and optionally from 0.1% to 25% by weight of the total composition of said second acid, or mixtures thereof, preferably from 0.1% to 20%, and more preferably from 0.1% to 10%.

6. A composition according to any of the preceding claims wherein said amine oxide is according to the formula $R_1R_2R_3NO$ wherein R1 is a saturated or unsaturated, linear or branched alkyl group of 1 to 30 carbon atoms, preferably of 8 to 20 carbon atoms, more preferably of 6 to 16, most preferably of 8 to 14, and wherein R2 and R3 are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups, or mixtures thereof.

7. A composition according to any of the preceding claims wherein said amine is according to the formula RR'R"N wherein R is a saturated or unsaturated linear or branched alkyl group of 1 to 30 carbon atoms, preferably of 8 to 20 carbon atoms, more preferably of 6 to 16, most preferably of 8 to 14 and wherein R' and R" are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups, or mixtures thereof.

8. A composition according to any of the preceding claims wherein said composition comprises from 0.1% to 5% by weight of the total composition of said amine oxide, or mixtures thereof, preferably from 0.1% to 3%, and from 0.1% to 5% by weight of the total composition of said amine, or mixtures thereof, preferably from 0.1% to 3%.

9. A composition according to any of the preceding claims wherein said composition has a pH below 3, preferably a pH of from 0.1 to 2.5 and more preferably of from 0.1 to 2.

10. A process of treating a hard-surface soiled by limescale-containing stains, wherein an acidic liquid composition according to any of the preceding claims is applied in its neat form or in diluted form, onto said surface, then left to act onto said surfaces, and then removed by rinsing.

11. The use, in an acidic limescale removal composition, of a surfactant system comprising an amine oxide according to the formula R1R2R3NO, wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and/or an amine according to the formula RR'R"N, wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms or hydrogen, to improve the greasy soap scum cleaning performance of said composition.

12. The use, in a liquid acidic composition, of a cationic surfactant according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion, R_1 is a C_8-C_{12} hydrocarbon chain and R_2, R_3 and R_4 are independently selected from H or C_1-C_4 hydrocarbon chains, preferably of lauryl trimethyl ammonium salts, to improve the limescale removal performance of said composition.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 20 1366

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP 0 666 305 A (PROCTER & GAMBLE) * claims * ---	1-11	C11D1/835 C11D3/20 C11D1/40
Y	GB 2 071 688 A (JEYES LTD) * the whole document * ---	1-11	C11D1/75 C11D3/34 C11D3/02
A	WO 96 13565 A (PROCTER & GAMBLE) * claims * ---	1,2,4, 6-11	
A	WO 95 33024 A (PROCTER & GAMBLE ET AL.) * claims 1,4,5 * ---	1,6-11	
D,A	EP 0 253 676 A (R & C PRODUCTS PTY LTD) * the whole document * ---	1-11	
A	EP 0 666 303 A (PROCTER & GAMBLE) * claims * ---	1-11	
Y	EP 0 666 304 A (PROCTER & GAMBLE) 9 August 1995 * claims 1-7 * ---	12	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
Y	COMUN. JORN. COM. ESP. DETERG. , vol. 21, 1990, SEVILLA ES, pages 191-206, XP000196765 ROERIG, H. ET AL: "Cationic surfactants in organic acid-based hard surface cleaners" * the whole document * -----	12	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	21 January 1997	Pelli Wablat, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EP 96201366

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid,

namely claims:

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

☒ LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

1. Claims 1-11: Refer to a composition containing a mixture of an amine oxide and an amine.

2. Claim 12: Relates to a quotenory ammonium salt. Furthermore the alkyl moieties are different.

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respects of which search fees have been paid,

namely claims:

☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims,

namely claims: