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(54) Acidic limescale removal compositions

(57) The present invention relates to a liquid acidic composition having a pH below 5 and comprising from 0.1% to 70% by weight of the total composition of an acid, and a surfactant system comprising a zwitterionic surfactant and a second surfactant selected from the group consisting 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,
- 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,
- a quaternary ammonium surfactant according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion, R_1 is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group of from 1 to 30 carbon atoms, and R_2, R_3 and R_4 are independently hydrogen, or saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms,
- and mixture thereof,

at a weight ratio of said zwitterionic surfactant to said second surfactant of at least 1:1. These 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 of the invention

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, i.e. soap scum and other greasy soils typically occurring in daily usage of bathrooms, e.g. body soils, and/or greasy soils typically occurring in daily usage of kitchens. Indeed, the presence of such greasy soap scum is detrimental to the limescale removal performance of liquid 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, such nonionic surfactants although being more desirable then other surfactants types that dramatically affect the limescale removal capacity of acids, are still not fully satisfactory to get optimum limescale removal performance when added in an acidic composition. Indeed, they 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 need for the development of limescale removal compositions with better performance in several respects including improved limescale removal performance and improved greasy soap scum cleaning 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 limescale removal performance and improved greasy soap scum cleaning performance.

It has now been found that the above object is met by formulating an acidic liquid composition (pH below 5) comprising at least an acid and a particular surfactant system, namely a zwitterionic surfactant and a second surfactant selected from the group consisting of an amine oxide, an amine, a quaternary ammonium surfactant as described herein and a mixture thereof, at a weight ratio of the rwitterionic surfactant to the second surfactant of at least 1:1. Indeed, it has been found that the compositions of the present invention comprising at least an acid, e.g., maleic acid alone or together with a second acid preferably sulphamic acid, and said surfactant system provides significantly improved limescale removal performance as well as improved greasy soap scum cleaning performance, as compared to the same compositions but with other surfactants like nonionic surfactants, (e.g. an alcohol ethoxylate (Dobanol® 91-8)) instead of said surfactant system according to the present invention.

In a broader aspect of the present invention, it has been found that the addition of a zwitterionic surfactant, 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 with another surfactant, e.g. a nonionic surfactant at the same total level of surfactant, this while providing excellent limescale removal performance. Thus, the present invention also encompasses the use of a zwitterionic surfactant, in a liquid acidic composition, to improve the greasy soap scum cleaning performance of said composition.

It has further surprisingly been found that the addition of a zwitterionic surfactant, in a liquid acidic composition, reduces or even prevents the deposition of soap scum on a hard-surface having first been treated with such a composition, resulting thereby in a longer lasting soap scum cleaning benefit. In other words, the housewife will have the advantage to delay the next cleaning operation. Thus, the present invention also encompasses the use of a zwitterionic surfactant, in a liquid acidic composition, to reduce deposition of soap scum on a hard surface after said surface has been first treated with said composition.

Background art

WO95/33024 discloses an aqueous viscous composition (pH = 0.5-7) comprising an amine oxide or amine and a secondary or primary monobranched alkyl sulphate or sulphonate in excess to said amine or amine oxide, a hydrotrope and an organic acid. No zwitterionic surfactants are disclosed.

GB 2071 688 discloses liquid acidic compositions comprising an inorganic acid and as a thickening agent a mixture of an amine or amine oxide with a cationic or nonionic surfactant. No zwitterionic surfactants are disclosed.

EP-A-265 979 discloses acidic thickened aqueous cleaning compositions comprising a disinfecting and/or oxidising agent, an organic anionic sulphonate selected from the group consisting of xylene sulphonate, cumene sulphonate and toluene sulphonate, and a surfactant selected from the group of (1) quaternary ammonium compounds wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group containing at least 12 carbon atoms and of (2) tertiary amine oxides wherein at least one of the hydrocarbon groups linked to the nitrogen is a linear or branched alkyl group containing at least 16 carbon atoms. No zwitterionic surfactants 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 zwitterionic surfactants 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 zwitterionic surfactants are disclosed.

Summary of the invention

The present invention is a liquid acidic composition having a pH below 5 and comprising from 0.1% to 70% by weight of the total composition of an acid or a mixture thereof, and a surfactant system comprising a zwitterionic surfactant and a second surfactant selected from the group consisting 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 containing from 1 to 30 carbon atoms,

- an amine according to the formula RR'R"N, wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 30 carbon atoms, or hydrogen,

- a quaternary ammonium surfactant according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion, R_1 is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, and R_2, R_3 and R_4 are each independently hydrogen, or saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 4 carbon atoms,

- and mixture thereof,

at a weight ratio of said zwitterionic surfactant to said second surfactant of at least 1:1.

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 zwitterionic surfactant as described herein, in a liquid acidic composition, to improve the greasy soap scum cleaning performance of said composition.

Finally, the present invention also encompasses the use of a zwitterionic surfactant as described herein, in a liquid acidic composition, to reduce deposition of soap scum on a hard surface after said surface has been first treated with said composition.

Detailed description of the invention

The liquid acidic compositions:

The liquid compositions of the present invention are acidic compositions. Accordingly, the compositions of the present invention are formulated at a pH below 5, preferably below 4, more preferably at a pH between 0 and 3, even more preferably at a pH between 0.1 and 2.5, even more preferably between 0.1 and 2, and most preferably at a pH between 0.3 and 1.5.

The liquid compositions according to the present invention are preferably aqueous compositions. Therefore, they typically comprise from 50% to 98% by weight of the total composition of water, preferably from 60% to 95% and more preferably from 70% to 90%.

The compositions according to the present invention are designed for removing limescale deposits. Thus, they comprise as a first essential feature an acid or a mixture thereof. Typically, the acids to be used herein may be any inorganic or organic acid well-known to those skilled in the art, or a mixture thereof. Suitable acids for use herein include maleic acid, citric acid, adipic acid, sulfamic acid, phosphoric acid, nitric acid, malic acid, sulfonic acid, sulphuric acid or their salts or mixtures thereof. Indeed, such acids can be used in their acidic form or in the form of their salts (mono-, di-, tri- salts) and in all their anhydrous and hydrated forms, or mixtures thereof. Such acids may typically be used in the form of their alkali metal salts (e.g. sodium salt, potassium salt, and then like) or their alkali hydrogen acid salts. The compositions according to the present invention comprise from 0.1% to 70% by weight of the total composition of an acid or a mixture thereof.

In a preferred embodiment herein the compositions of the present invention comprise at least 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.

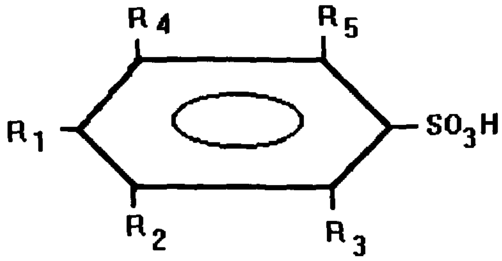
In another embodiment of the present invention, a second acid is added on top of said maleic acid. Said second acid is desired to strengthen the limescale removal performance. Preferably the second acids to be used herein which are particularly efficient to remove limescale on many surfaces, have their 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 is sulphamic acid. An advantage of a preferred embodiment of the present invention wherein sulphamic acid is added on top of another organic or inorganic acid or mixture thereof such as maleic acid, in the acidic compositions of the present invention, is improved skin mildness of said compositions. In other words, the addition of sulphamic acid to a given organic and/or inorganic acid-containing compositions improves the skin safety profile of said compositions. Indeed, less skin irritation is perceived by the user when its skin comes into contact with the compositions of the present invention comprising sulphamic acid on top of another acid (e.g. maleic acid) as compared to the same compositions but without sulphamic acid. In other words, the skin will be less subject to become inflamed, red, sore and/or itchy when in contact with those acidic compositions of the present invention comprising sulfamic acid on top of another acid otherwise perceived to be more irritant to skin.

Other suitable second acids 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 alkyl chain or only one. Indeed, such arylsulphonic acids are particularly effective at removing limescale, which is not the case for their longer alkyl chain homologues. Also, such 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 %, 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, citric acid or mixtures thereof, more preferred are sulphamic acid, sulphuric acid, benzene sulphonic acid, citric 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 liquid acidic compositions of the present invention comprise as a second essential feature a surfactant system comprising a zwitterionic surfactant and a second surfactant as described herein, at a weight ratio of the zwitterionic surfactant to the second surfactant of at least 1:1.

The zwitterionic surfactants have the advantage when added in an acidic composition comprising at least an acid, that the limescale removal performance provided by said composition is equivalent to the limescale removal performance observed with the same acidic composition without any surfactant. Indeed, it has been found that in contrast to other surfactants like nonionic surfactants which when added in a given acidic composition comprising at least an acid, decrease the limescale removal performance of said composition, the addition of zwitterionic surfactants to an acidic limescale removal composition maintains the limescale removal performance of said composition. It is speculated that in contrast to other surfactants like nonionic surfactants that tend to put themselves with a very tight packing at the liquid-solid interface, i.e., at the interface between the acidic composition and the limescale deposits, thereby limiting the limescale removal action of the acids, the zwitterionic surfactants thanks to their double charged functional groups do not form a tight packing at the liquid-solid interface. Thus, the addition of zwitterionic surfactants, in a liquid acidic composition, does not reduce the limescale removal action of the acids present in said composition.

Also, the addition of a zwitterionic surfactant as described herein, in a liquid acidic composition provides not only outstanding limescale removal performance, but also 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 at same total level of surfactants. Thus, in a broader aspect the present invention also encompasses the use, in an acidic liquid limescale removal composition, of a zwitterionic surfactant, to improve the greasy soap scum cleaning performance of said composition.

Although not wishing to be bound by theory, it is further speculated that the zwitterionic surfactants have the property of adsorbing to a hard-surface being first treated therewith, in such a manner that a certain amount of zwitterionic surfactants is left behind on the treated surface. In fact, it is believed that the zwitterionic surfactants left behind on the treated surface, especially the sulfobetaine surfactants, act as lime soap dispersing agents. In presence of soap molecules (anionic surfactants) Ca cations coming from tap water are complexed by soap itself leading to formation of "soap scum" (also called "lime soap", i.e., insoluble organic calcium salts such as calcium stearate or calcium oleate) which precipitates. A lime soap dispersing agent is a compound that allows, thanks to its large head group, the formation of mixed micelles with soap molecules, thus avoiding formation and, then, precipitation of insoluble organic calcium salts.

Thus, it has been found that the addition of a zwitterionic surfactant, preferably a sulfobetaine surfactant, in a liquid acidic composition, reduces or even prevents the deposition of soap scum on a hard-surface after the surface has been first treated with said composition, thereby ensuring long lasting soap scum cleaning benefit.

Suitable zwitterionic surfactants to be used herein contain at least one anionic and one cationic group in the molecule. Depending on the pH and in relation to their isoelectric area, they behave more cationically or more anionically, but usually exhibit both anionic and cationic type properties simultaneously over a wide pH range. The typical cationic group can be a secondary or tertiary ammonium group (so called "weak nitrogen zwitterionics") or a quaternary ammonium group (so called "betaines"), although other positively charged groups like phosphonium, imidazolium and sulfonium groups can be used. The main difference is that betaines carry a positive charge over the whole pH range, whereas weak nitrogen zwitterionics carry a positive charge only in acidic pH. 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 preferred zwitterionic surfactants for use herein (i.e., betaine and/or sulfobetaine) is:

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

wherein R_1 is a hydrophobic group; R_2 is hydrogen, C_1-C_6 alkyl, hydroxy alkyl or other substituted C_1-C_6 alkyl group; R_3 is C_1-C_6 alkyl, hydroxy alkyl or other substituted C_1-C_6 alkyl group which can also be joined to R_2 to form ring structures with the N, or a C_1-C_6 carboxylic acid group or a C_1-C_6 sulfonate group; 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 10 carbon atoms; and X is the hydrophilic group which is a carboxylate or sulfonate group, preferably sulfonate group.

Preferred hydrophobic groups R_1 are aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chains that can contain linking groups such as amido groups, ester groups. More preferred R_1 is an alkyl group containing from 1 to 24 carbon atoms, preferably from 8 to 18, and more preferably from 10 to 16. These simple alkyl groups are preferred for cost and stability reasons. However, the hydrophobic group R_1 can also be an amido radical of the formula R_a-C(O)-NR_b-$(C(R_c)_2)_m$, wherein R_a is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain containing from 8 up to 20 carbon atoms, preferably an alkyl group containing from 8 up to 20 carbon atoms, preferably up to 18, more preferably up to 16, R_b is either a hydrogen, a short chain alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl or hydrogen, R_c is selected from the group consisting of hydrogen and hydroxy groups, and m is from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R_c)_2)$ moiety.

Preferred R_2 is hydrogen, or an alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl. Preferred R_3 is a C_1-C_4 carboxylic acid group, a C1-C4 sulfonate group, or an alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl. Preferred R_4 is $(CH2)_n$ wherein n is an integer from 1 to 10, preferably from 1 to 6, more preferably from 1 to 3.

Some common examples of betaine/sulphobetaine are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference.

Examples of particularly suitable alkyldimethyl betaines include coconut-dimethyl betaine, lauryl dimethyl betaine, decyl dimethyl betaine, 2-(N-decyl-N, N-dimethyl-ammonia)acetate, 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine. For example Coconut dimethyl betaine is commercially available from Seppic under the trade name of Amonyl 265®. Lauryl betaine is commercially available from Albright & Wilson under the trade name Empigen BB/L®.

A further example of betaine is Lauryl-immino-dipropionate commercially available from Rhone-Poulenc under the trade name Mirataine H2C-HA®.

Particularly preferred zwitterionic surfactants for use in the acidic compositions of the present invention are the sulfobetaine surfactants, as they deliver optimum limescale removal benefits and greasy soap scum cleaning benefits.

Examples of particularly suitable sulfobetaine surfactants include cocoamido propyl hydroxy sulfobetaines which are commercially available from Rhone Poulenc and Witco, under the trade name of Mirataine CBS® and Rewoteric AM CAS 15® respectively.

Further examples of amidobetaines/amidosulfobetaines include cocoamidoethylbetaine, cocoamidopropyl betaine or C10-C14 fatty acylamidopropylene(hydropropylene)sulfobetaine. For example C10-C14 fatty acylamidopropylene(hydropropylene)sulfobetaine is commercially available from Sherex Company under the trade name "Varion CAS® sulfobetaine".

The compositions of the present invention comprise from 0.01% to 20% by weight of the total composition of a zwitterionic surfactant or a mixture thereof, preferably from 0.1% to 10% and more preferably from 0.1% to 5%.

The second surfactant suitable to be used herein has the particularity to further boost the greasy soap scum cleaning performance of the zwitterionic surfactant while not compromising on the limescale removal performance. Suitable second surfactants to be used herein are selected from the group consisting of amine oxides as described hereinafter, amines as described hereinafter and/or quaternary ammonium surfactants as described hereinafter.

Suitable amine oxides for use 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 group containing from 1 to 30 carbon atoms, and preferably 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 containing from 1 to 30 carbon atoms, preferably from 8 to 20 carbon atoms, more preferably from 6 to 16, most preferably from 8 to 14, and wherein R2 and R3 are independently substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 4 carbon atoms, preferably 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®).

Suitable amines for use herein are according to the following formula RR'R"N wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, and preferably from 1 to 20 carbon atoms and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups containing 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 containing from 1 to 30 carbon atoms, preferably from 8 to 20 carbon atoms, more preferably from 6 to 16, most preferably from 8 to 14 and wherein R' and R" are independently substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 4 carbon atoms, preferably 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®.

Suitable quaternary ammonium surfactants for use herein are according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion such as a halogen, methyl sulphate, methyl sulphonate, or hydroxide, R_1 is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, preferably from 12 to 20, more preferably from 8 to 20 and R_2, R_3 and R_4 are independently hydrogen, or saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 4 carbon atoms, preferably from 1 to 3 and more preferably methyl. In highly preferred quaternary ammonium surfactants herein 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 quaternary ammonium surfactants are myristyl trimethylammonium methyl sulphate, cetyl trimethylammonium methyl sulphate, 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. Such trimethyl quaternary ammonium surfactants may be commercially available from Hoechst, or from Albright & Wilson under the trade name Empigen CM®.

The compositions of the present invention comprise from 0.01% to 10% by weight of the total composition of said second surfactant or a mixture thereof, preferably from 0.04% to 5%, more preferably from 0.06% to 3% and most preferably from 0.08% to 1.5%.

In a preferred embodiment the total level of said surfactant system in the compositions of the present invention is typically from 0.1% to 30% by weight of the total composition, preferably from 0.1% to 10%, more preferably from 0.2% to 5% and most preferably from 0.5% to 3%.

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.

It has unexpectedly been found that by combining a zwitterionic surfactant with the second surfactant, i.e. an amine oxide and/or amine and/or a quaternary ammonium surfactant as described herein, at a weight ratio of the zwitterionic surfactant to the second surfactant of at least 1:1, in an acidic composition comprising an acid or a mixture thereof, outstanding limescale removal performance as well as outstanding greasy soap scum cleaning performance is delivered.

In a preferred embodiment of the present invention the zwitterionic surfactant is in excess to the second surfactant to provide optimum limescale removal performance, i.e, comparable to the limescale removal performance of the same composition without any surfactant, while delivering also effective grease soap scum cleaning performance. Accordingly the weight ratio of the zwitterionic surfactant to the second surfactant is preferably at least 2:1, more preferably from 10:1 to 2.5:1 and most preferably from 6:1 to 2.5:1.

In a preferred embodiment of the present invention wherein the acidic composition of the present invention further comprises a perfume, the presence of the second surfactant not only boost the greasy soap scum cleaning performance of the zwitterionic surfactant while not compromising the outstanding limescale removal performance delivered due to the presence of the zwitterionic surfactant, but also helps dissolution of the perfume in said composition, thereby improving the physical stability of an acidic perfume-containing composition according to the present invention. In other words, the presence of the second surfactant allows dissolution of the perfume in the acidic compositions according to the present invention at lower total level of surfactants, as compared to the level of zwitterionic surfactants that would be needed when used alone in absence of said second surfactant. Another advantage of the present invention is that cost effective compositions are provided that have all the technical features described herein.

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

Optional ingredients:

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

Surfactants

In the preferred embodiment of the present invention the compositions herein do not contain any additional surfactant on top of the surfactant system described herein. However, other surfactants may be added depending on the end use desired, for example, when it is desired to provide viscosity to the acidic compositions of the present invention.

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, other cationic or amphoteric surfactants. It is also possible to use mixtures of such surfactants without departing from the spirit of the present invention.

Nonionic surfactants and/or anionic surfactants may be added in the compositions of the present invention although this execution is not preferred when considering only the limescale removal ability of the compositions. Indeed the addition of such surfactants may decrease the limescale removal profile of the compositions 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 19. 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.

Suitable alkyl sulphonates for use herein include water-soluble salts or acids of the formula RSO_3M wherein R is a C_6-C_{20} linear or branched, saturated or unsaturated alkyl group, preferably a C_{12}-C_{18} alkyl group and more preferably a C_{14}-C_{16} alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Suitable alkyl aryl sulphonates for use herein include water- soluble salts or acids of the formula RSO_3M wherein R is an aryl, preferably a benzyl, substituted by a C_6-C_{20} linear or branched saturated or unsaturated alkyl group, preferably a C_{12}-C_{18} alkyl group and more preferably a C_{14}-C_{16} alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

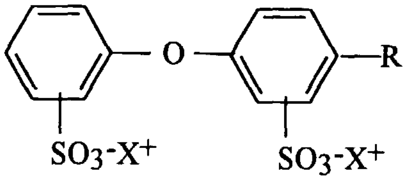
By "secondary C6-C20 alkyl or C6-C20 alkyl aryl sulphonates", it is meant herein that in the formula as defined above, the SO3M or aryl-SO3M group is linked to a carbon atom of the alkyl chain being placed between two other carbons of the said alkyl chain (secondary carbon atom).

An example of a C14-C16 alkyl sulphonate is Hostapur ® SAS available from Hoechst. An example of commercially available alkyl aryl sulphonate is Lauryl aryl sulphonate from Su.Ma. Particularly preferred alkyl aryl sulphonates are alkyl benzene sulphonates commercially available under trade name Nansa® available from Albright&Wilson.

Suitable alkyl sulphate surfactants for use herein are according to the formula R_1SO_4M wherein R_1 represents a hydrocarbon group selected from the group consisting of straight or branched alkyl radicals containing from 6 to 20 carbon atoms and alkyl phenyl radicals containing from 6 to 15 carbon atoms in the alkyl group. M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Suitable alkyl alkoxylated sulphate surfactants for use herein are according to the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_6-C_{20} alkyl or hydroxyalkyl group having a C_6-C_{20} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate, C_{12}-$C_{18}E(1.0)M)$, C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12}-$C_{18}E(2.25)M)$, C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate C_{12}-$C_{18}E(3.0)$, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate C_{12}-$C_{18}E(4.0)M)$, wherein M is conveniently selected from sodium and potassium.

Suitable C_6-C_{20} alkyl alkoxylated linear or branched diphenyl oxide disulphonate surfactants for use herein are according to the following formula:



wherein R is a C_6-C_{20} linear or branched, saturated or unsaturated alkyl group, preferably a C_{12}-C_{18} alkyl group and more preferably a C_{14}-C_{16} alkyl group, and X+ is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc). Particularly suitable C_6-C_{20} alkyl alkoxylated linear or branched diphenyl oxide disulphonate surfactants to be used herein are the C12 branched di phenyl oxide disulphonic acid and C16 linear di phenyl oxide disulphonate sodium salt respectively commercially available by DOW under the trade name Dowfax 2A1® and Dowfax 8390®.

Other anionic surfactants useful herein include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C_{14-16} methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO\text{-}M^+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

Preferred anionic surfactants herein include the primary and secondary C_6-C_{20} alkyl suplonates and the primary and secondary C_6-C_{20} alkyl aryl sulphonates or a mixture thereof.

Polymers

The liquid acidic compositions of the present invention may comprise an acid-stable polymer or a mixture thereof. Suitable acid-stable polymers to be used herein including polycarboxylate polymers, sulphonated polystyrene polymers, vinylpyrrolidone homopolymer or copolymers, polyalkoxylene glycols, polysaccharide polymers or a mixture thereof. Such polymers may be desired as their addition in the acidic compositions of the present invention deliver improved skin mildness and improved shine while not compromising on the limescale removal performance and/or greasy soap scum removal performance of said compositions. Typically, the compositions herein comprise up to 5% by weight of the total composition of an acid-stable polymer or a mixture thereof, preferably from 0.001% to 3% more preferably from 0.002% to 2% and most preferably from 0.01% to 1%.

By "acid-stable", it is meant herein that the polymers for use herein allow that the chemical parameters of the acidic compositions according to the present invention, e.g. the composition pH and/or the acidity reserve, do not change when the composition is stored in rapid aging test (RAT) at 50°C for 6 days.

Suitable polycarboxylate polymers for use herein are polymers comprising monomeric units selected from the group consisting of unsaturated carboxylic acids such as acrylic acid, polycarboxylic acids, sulphonic acids, phosphonic acids and mixtures thereof. Copolymerisation of the above monomeric units among them or with other co-monomers such as maleic anhydride, ethylene or propylene are also suitable. When used, maleic anhydride will acts as a source of additional carboxylic groups, whilst ethylene and propylene will act as diluents.

The molecular weight per carboxylate group of monomers containing a carboxylate group typically varies from 20 to 200, preferably from 40 to 150, more preferably from 50 to 125. Preferred polymers for use herein have a total molecular weight of from 2,000 to 4,500,000, preferably from 10,000 to 4,000,000. Most preferred polymers for use herein contain from 0.5% to 4% by weight of a cross-linking agent, wherein the cross-linking agent tends to interconnect linear strands of the polymers to form the resulting cross-linked products. Suitable cross-linking agents include the polyalkenyl polyethers.

Preferred polycarboxylate polymers for use herein are the polyacrylate polymers. Typically acrylic/maleic-based copolymers may be used as a preferred polyacrylate polymer. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 1,000,000, more preferably from about 5,000 to 100,000, most preferably from about 10,000 to 80,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982. Particularly preferred is a copolymer of maleic / acrylic acid with an average molecular weight of about 70,000. Such copolymers are commercially available from BASF under the trade name Sokalan CP5®.

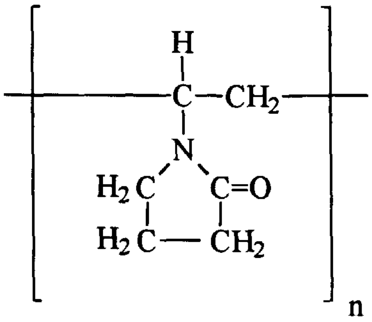
Other preferred polyacrylate polymers are the copolymer of acrylic acid and alkyl (C_5-C_{10}) acrylate, commercially available under the tradename Carbopol ® 1623, Carbopol® 695 from BF Goodrich. Commercially available polymers of the polyacrylate type further include those sold under the trade names Carbopol®, Acrysol® ICS-1, Polygel®, and Sokalan®.

Two different types of sulfonated polystyrene polymers are useful herein. The first type is a sulfonated homopolymer of styrene. The second type is a sulfonated interpolymer of styrene with an ethylenically unsaturated comonomer. The useful compounds herein include the partially or fully neutralized salts of either the sulfonated polystyrene or the sulfonated styrene interpolymers, i.e. the soluble salts of these polymers, wherein the sulfonic acid groups are partially or fully neutralized.

Suitable ethylenically unsaturated comonomer units which can be copolymerized with styrene to make the interpolymers suitable for sulfation include acrylic and methacrylic esters of aliphatic alcohols such as methyl, ethyl, butyl and 2-ethyl hexyl alcohols, acrylic acid, acrylonitrile, methacrylonitrile, dibutyl maleate, vinylidene chloride and the like. Particularly preferred ethylenically unsaturated monomers for use herein include ethylene, propylene, styrene, vinyl naphthalene, acrylic acid and maleic anhydride.

Sulphonated styrene homopolymers suitable for use herein are commercially available under the trade name Versaflex® from National Starch. Most suitable polymers and copolymers for use herein will be water soluble, and the molecular weight for these polymers is preferably between 5000 and 10,000,000, most preferably between 50,000 and 1,000,000.

Suitable vinylpyrrolidone homopolymers for use herein are homopolymers of N-vinylpyrrolidone having the following repeating monomer:



wherein n (degree of polymerisation) is an integer of from 10 to 1,000,000, preferably from 20 to 100,000, and more preferably from 20 to 10,000.

Accordingly, suitable vinylpyrrolidone homopolymers ("PVP") for use herein have an average molecular weight of from 1,000 to 100,000,000, preferably from 2,000 to 10,000,000, more preferably from 5,000 to 1,000,000, and most preferably from 50,000 to 500,000.

Suitable vinylpyrrolidone homopolymers are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15® (viscosity molecular weight of 10,000), PVP K-30® (average molecular weight of 40,000), PVP K-60® (average molecular weight of 160,000), and PVP K-90® (average molecular weight of 360,000). Other suitable vinylpyrrolidone homopolymers which are commercially available from BASF Cooperation include Sokalan HP 165® and Sokalan HP 12®; vinylpyrrolidone homopolymers known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

Suitable copolymers of vinylpyrrolidone for use herein include copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof.

The alkylenically unsaturated monomers of the copolymers herein include unsaturated dicarboxylic acids such as maleic acid, chloromaleic acid, fumaric acid, itaconic acid, citraconic acid, phenylmaleic acid, aconitic acid, acrylic acid, N-vinylimidazole and vinyl acetate. Any of the anhydrides of the unsaturated acids may be employed, for example acrylate, methacrylate. Aromatic monomers like styrene, sulphonated styrene, alpha-methyl styrene, vinyl toluene, t-butyl styrene and similar well known monomers may be used.

The molecular weight of the copolymer of vinylpyrrolidone is not especially critical so long as the copolymer is water-soluble, has some surface activity and is adsorbed to the hard-surface from the liquid composition or solution (i.e. under dilute usage conditions) comprising it in such a manner as to increase the hydrophilicity of the surface. However, the preferred copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers or mixtures thereof, have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 200,000.

For example particularly suitable N-vinylimidazole N-vinylpyrrolidone polymers for use herein have an average molecular weight range from 5,000-1,000,000, preferably from 5,000 to 500,000, and more preferably from 10,000 to 200,000. The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113,"Modern Methods of Polymer Characterization".

Such copolymers of N-vinylpyrrolidone and alkylenically unsaturated monomers like PVP/vinyl acetate copolymers are commercially available under the trade name Luviskol® series from BASF.

The copolymers of vinylpyrrolidone for use in the compositions of the present invention also include quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers. The preferred quaternized or unquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers for use herein have a molecular weight of between 1,000 and 1,000,000, preferably between 10,000 and 500,000 and more preferably between 10,000 and 100,000. Such vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers are commercially available under the name copolymer 845®, Gafquat 734®, or Gafquat 755® from ISP Corporation, New York, NY and Montreal, Canada or from BASF under the tradename Luviquat®.

Suitable polyalkoxylene glycols for use herein have the following formula:

$$\text{H-O-(CH}_2\text{-CHRO)}_n\text{-H},$$

wherein R is hydrogen or a linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, preferably R is hydrogen, or a linear or branched alkyl group, alkenyl group or aryl group having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 8, and most preferably R_2 is methyl, or hydrogen. Preferably n is an integer from 5 to 1000, more preferably from 10 to 100, even more preferably from 25 to 60 and most preferably from 30 to 50.

The preferred polyalkoxylene glycols to be used according to the present invention have a molecular weight of at least 200, more preferably from 400 to 5000 and most preferably from 800 to 3000.

Preferred polyalkoxylene glycols are polyethylene glycols like polyethylene glycol (MW 2000).

Suitable polysaccharide polymers for use herein include substituted cellulose materials like carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan and naturally occurring polysaccharide polymers like xanthan gum, guar gum, locust bean gum, tragacanth gum or derivatives thereof, or mixtures thereof. Particularly preferred polysaccharide polymers to be used herein are xanthan gum and derivatives thereof. Xanthan gum and derivatives thereof may be commercially available for instance from Kelco under the trade name Keltrol RD®, Kelzan S ® or Kelzan T®.

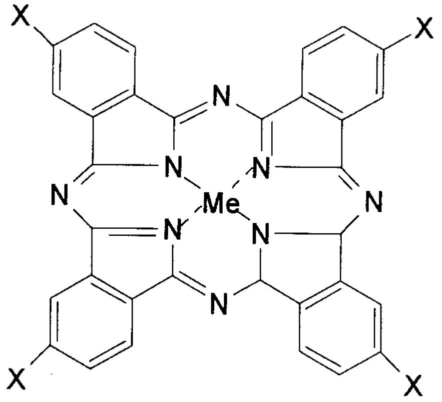
Preferred acid-stable polymers to be used herein are the sulphonated polystyrene polymers and/or the vinylpyrrolidone homopolymers.

In the embodiment of the present invention wherein the compositions herein further comprise such an acid-stable polymer said compositions are typically thickened liquid acidic compositions. Indeed, the addition of the acidic-stable polymers in the compositions of the present invention increases the viscosity of said compositions. Thus, in the embodiment of the present invention wherein such an acid-stable polymer is present in the compositions of the present invention, they typically have a viscosity of from 10 m Pa s to 1500 m Pa s at 20°C, preferably from 10 m Pa s to 600 m Pa s, more preferably from 20 m Pa s to 400 m Pa s, and most preferably from 30 m Pa s to 200 m Pa s, when measured with a Carri-med rheometer CLS 100® by TA Instruments at 5 N/m2 with a 4 cm diameter cone spindle.

Dyes

The liquid compositions according to the present invention may be colored. Accordingly, they may comprise a dye or a mixture thereof. Suitable dyes to be used herein are acid-stable dyes. By "acid-stable", it is meant herein a compound which is chemically and physically stable in the acidic environment of the compositions herein. Suitable dyes to be used herein include α or β metal phthalocyanines and/or trimethyl methane dyes.

The α or β metal phthalocyanine dyes suitable to be used in the compositions of the present invention are light-fast organic pigments with four isoindole groups, $(C_6H_4)C_2N$, linked by four nitrogen atoms to form a conjugated chain. Their general structure is the following:



where the substituent X may be one of the following groups :H, Cl, HSO_3, COO-M+, Br, NO_2, OCH_3 or a C_1 to C_{10} alkyl group and where Me is copper, chromium, vanadium, magnesium, nickel, platinum, aluminium, cobalt, lead, barium or zinc. Preferred α or β metal phthalocyanine dyes to be used herein are α or β copper phthalocyanine dyes.

Examples of such α copper phthalocyanine dyes to be used herein are copper phthalocyanine (X = H, blue colour) commercially available under the name *UNISPERSE Blue B-E®* from Ciba-Geigy, or *Cosmenyl blue A2R®* from Hoechst, or *Pigmosol blue 6900®* from BASF, or chlorinated copper phthalocyanine (X = Cl, green colour) commercially available under the name *Pigmosol Green 8730®* from BASF.

Examples of trimethyl methane dyes are commercially available from Hoescht under the name *Vitasyn®* or from BASF under the name *Acid Blue®*.

Typically, the compositions of the present invention may comprise up to 0.2% by weight of the total composition of a dye or a mixture thereof, preferably from 0.001% to 0.015% and more preferably from 0.001% to 0.012%.

Perfumes

In one embodiment of the present invention, the compositions as described hereinbefore further comprise a perfume or a mixture thereof. An advantage of the acidic compositions of the present invention is that they are physically stable in the presence of perfumes, even the presence of high levels of perfumes. Indeed the second surfactants herein helps the dissolution of the perfume in the acidic compositions herein.

The perfume ingredients and compositions suitable to be used herein are the conventional ones known in the art. Suitable perfume compounds and compositions can be found in the art including U.S. Pat. Nos.: 4,145,184, Brain and Cummins, issued March 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 and 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, ciscitral (neral), citronellal, citronellol, citronellyl acetate, para-cymene, decanal, dihydrolinalool, dihydromyrcenol, dimethyl phenyl carbinol, eucaliptol, cedrol, 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 carbinyl acetate, laevo-menthyl acetate, menthone, iso-menthone, mycrene, myrcenyl acetate, myrcenol, nerol, neryl acetate, nonyl acetate, phenyl ethyl alcohol, alpha-pinene, 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 carbinyl acetate, ethyl vanillin, eugenol, iso-eugenol, for acetate, heliotropine, 3-cis-hexenyl salicylate, hexyl salicylate, lilial (para-tertiarybutyl-alpha-methyl hydrocinnamic aldehyde), gamma-methyl ionone, nerolidol, patchouli alcohol, phenyl hexanol, beta-selinene, trichloromethyl phenyl carbinyl 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.

The liquid acidic compositions according to the present invention comprise up to 3% by weight of the total composition of a perfume or a mixture thereof, preferably of from 0.05% to 2% and more preferably of from 0.1% to 1%.

Packaging form of the liquid acidic compositions:

The liquid acidic compositions according to the present invention may be packaged in a variety of suitable detergent packaging known to those skilled in the art.

For example in the embodiment of the present invention wherein the compositions of the present invention further comprise an acid-stable polymer, they may be easily dispensed onto the surface to be treated via a spray-type dispenser such as for instance a trigger-sprayer. Suitable spray-type dispensers to be used according to the present invention include manually operated foam trigger-type dispensers sold for example by Specialty Packaging Products, Inc. or Continental Sprayers, Inc. These types of dispensers are disclosed, for instance, in US-4,701,311 to Dunnining et al. and US-4,646,973 and US-4,538,745 both to Focarracci. Particularly preferred to be used herein are spray-type dispensers such as T 8500® or T 8900® commercially available from Continental Spray International or T 8100® commercially available from Canyon, Northen Ireland. In such a dispenser the liquid composition is divided in fine liquid droplets resulting in a spray that is directed onto the surface to be treated. Indeed, in such a spray-type dispenser the composition contained in the body of said dispenser is directed through the spray-type dispenser head via energy communicated to a pumping mechanism by the user as said user activates said pumping mechanism. More particularly, in said spray-type dispenser head the composition is forced against an obstacle, e.g. a grid or a cone or the like, thereby providing shocks to help atomise the liquid composition, i.e. to help the formation of liquid droplets.

Process for treating surfaces:

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 other 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.

Limescale removal performance test method:

The limescale removal capacity of a composition according to the present invention may be evaluated by soaking a marble block (marble blocks are chemically speaking very similar to limescale, i.e. they are essentially made of calcium carbonate) into 20 g of this composition. The marble is weighed before and after the experiment, and the performance is expressed in grams of marble block dissolved over time. Alternatively, limescale removal performance can also be evaluated by detecting the release of CO2.

Greasy soap scum cleaning performance test method:

In this test method enamel white tiles (typically 24 cm * 4 cm) are covered with typical greasy soap scum soils mainly based on calcium stearate and artificial body soils commercially available (e.g. 0.3 grams with a sprayer). The soiled tiles are then dried in an oven at a temperature of 140 °C for 30 minutes and then aged overnight at room temperature (around 15°C-20°C). Then the soiled tiles are treated with a Spontex® sponge impregnated with the liquid acidic composition of the present invention (e.g. 5 grams). The ability of the composition to remove greasy soap scum is measured through the number of strokes needed to perfectly clean the surface. The lower the number of strokes, the higher the greasy soap scum cleaning ability of the composition.

Test method to evaluate lime soap dispersing ability of a compound:

This test method can be carried out as described herein: 5 ml of sodium oleate (0.5g/100ml) is pipetted into a test tube and an arbitrary amount of lime soap dispersing agent (e.g. 5 ml of 0.25g/100ml solution) is added, followed by 10ml of hard water (60% calcium and 40% magnesium totalling 1g/l calculated as Ca CO3 = 70° English hardness). The volume is then made up to 30ml with distilled water. The test tube is stoppered and inverted 20 times, and then allowed to stand for 30 seconds after which the condition of the lime soap particles is observed. The test is repeated to determine the minimum amount of lime soap dispersing agent (LSDA) in gram (A in the following equation) to prevent formation of a coagulated precipitate, i.e. the lime soap particles. The solution becomes translucent just before this end point. The measurement of lime soap dispersing ability is given by the following formula:

$$\text{\% lime soap dispersing ability} = \frac{\text{A (in grams)}}{\text{0.025 (weight of sodium oleate)}} \times 100$$

The lower the % lime soap dispersing ability, the better the LSDA ability of said compound. This test method, also called "Borghetty and Bergman test" can be found in literature (JAOCS vol 27 pag. 88-90).

The present invention is further illustrated by the following examples.

Examples

These compositions were made comprising the listed ingredients in the listed proportions (weight %).

Compositions

Ingredients: (% by weight)	I	II	III	IV	V	VI
Maleic acid	10	12	10	10	10	10
Sulphamic acid	2	-	2	2	2	2
Mirataine CBS® (*)	1	0.9	0.8	-	1	-
Rewoteric AM CAS 15® (*)	-	-	-	1	-	0.9
C12/C14 amine oxide	0.3	0.3	0.3	0.4	-	-
C12 dimethyl amine	-	-	-	-	0.3	0.3
Waters & Minors (perfumes,dyes)	--------------------- up to 100 -------------------					

Ingredients: (% by weight)	VII	VIII	IX	X	XI	XII
Maleic acid	10	-	10	14	8	10
Sulphamic acid	-	2	2	-	2	2
Citric acid	5	10	-	-	-	-
Mirataine CBS® (*)	1	0.9	0.8	-	1	-
Rewoteric AM CAS 15® (*)	-	-	-	1	-	0.9
C12/C14 amine oxide	0.3	0.3	0.3	0.4	-	-
C12 tertiary amine	-	-	-	-	-	0.1
C16 trimethyl ammonium Chloride	-	-	-	-	0.4	0.2
Polystyrene sulphonate	-	0.03	-	0.04	-	-
Polyvinyl pyrrolidone	0.03	-	0.05	-	-	0.04
Waters & Minors	--------------------- up to 100 -------------------					

Ingredients: (% by weight)	XIII	XIV	XV	XVI	XVII	XVIII
Maleic acid	10	-	12	8	10	10
Sulphamic acid	-	2	-	2	2	2
Citric acid	5	10	-	-	-	-
Mirataine CBS® (*)	1	0.9	0.8	-	1	-
Rewoteric AM CAS 15® (*)	-	-	-	1	-	0.9
C12/C14 amine oxide	0.1	-	0.1	-	-	-
C12 tertiary amine	-	-	-	0.3	-	0.1
LTAB (**)	0.2	0.3	0.3	-	0.4	0.2
Waters & Minors	------------------- up to 100 -------------------					

(*) Mirataine CBS® and Rewoteric AM CAS 15® are examples of cocoamidopropyl hydroxy sulphobetaine supplied respectively by Rhone-Poulenc and Witco.

(**) 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. These compositions also ensure long lasting soap scum cleaning to a surface having been treated therewith.

Claims

1. A liquid acidic composition having a pH below 5, and comprising from 0.1% to 70% by weight of the total composition of an acid, and a surfactant system comprising a zwitterionic surfactant and a second surfactant selected from the group consisting 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 containing from 1 to 30 carbon atoms,

   - an amine according to the formula RR'R"N, wherein R is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, and wherein R' and R" are independently saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 30 carbon atoms, or hydrogen,

   - a quaternary ammonium surfactant according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion, R_1 is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, and R_2, R_3 and R_4 are independently hydrogen, or saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 4 carbon atoms,

- and a mixture thereof,

at a weight ratio of said zwitterionic surfactant to said second surfactant of at least 1:1.

2. A composition according to claim 1 wherein said acid is an organic or inorganic acid or a mixture thereof.

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 a mixture thereof and preferably sulphamic acid.

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 zwitterionic surfactant is according to the formula:

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

wherein R_1 is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain that can contain linking groups such as amido groups, ester groups, preferably an alkyl group containing from 1 to 24 carbon atoms, more preferably from 8 to 18, or an amido radical of the formula $R_a\text{-C(O)-NR}_b\text{-}(C(R_c)_2)_m$, wherein R_a is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain containing from 8 up to 20 carbon atoms, R_b is either a hydrogen a short chain alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl or hydrogen, R_c is selected from the group consisting of hydrogen and hydroxy groups, and m is from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R_c)_2)$ moiety;

R_2 is hydrogen, C_1-C_6 alkyl, hydroxy alkyl or other substituted C_1-C_6 alkyl group;

R_3 is C_1-C_6 alkyl, hydroxy alkyl or other substituted C_1-C_6 alkyl group which can also be joined to R_2 to form ring structures with the N, or a C_1-C_6 carboxylic acid group or a C_1-C_6 sulfonate group;

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 10 carbon atoms;

and X is the hydrophilic group which is a carboxylate or sulfonate group.

7. 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, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, preferably from 8 to 20 carbon atoms, more preferably from 6 to 16, most preferably from 8 to 14, and wherein R2 and R3 are independently substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 4 carbon atoms, preferably 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 amine is according to the formula RR'R"N wherein R is a saturated or unsaturated linear or branched alkyl group containing from 1 to 30 carbon atoms, preferably from 8 to 20 carbon atoms, more preferably from 6 to 16, most preferably from 8 to 14 and wherein R' and R" are independently substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups, or a mixture thereof.

9. A composition according to any of the preceding claims wherein said quaternary ammonium surfactant is according to the formula $R_1R_2R_3R_4N^+ X^-$, wherein X is halogen, methyl sulphate, methyl sulphonate, or hydroxide, R_1 is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 12 to 20 carbon atoms, more preferably from 8 to 20, and R_2, R_3 and R_4 are each independently hydrogen, or saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 3 carbon atoms, and more preferably methyl, or a mixture thereof.

10. A composition according to any of the preceding claims wherein said composition comprises from 0.1% to 20% by weight of the total composition of said zwitterionic surfactant, or a mixture thereof, preferably from 0.1% to 10%, and from 0.01% to 10% by weight of the total composition of said second surfactant or a mixture thereof, preferably from 0.04% to 5% and more preferably from 0.06% to 3%.

11. A composition according to any of the preceding claims wherein the weight ratio of said zwitterionic surfactant to said second acid is at least 2:1, preferably from 2.5:1 to 10:1, more preferably from 2.5:1 to 6:1

12. A composition according to any of the preceding claims which has a pH below 4, preferably a pH of from 0.1 to 2.5 and more preferably of from 0.1 to 2.

13. A composition according to any of the preceding claims which further comprises an acid-stable polymer or a mixture thereof, up to a level of 5% by weight of the total composition, said polymer being preferably a polycarboxylate polymer, a sulphonated polystyrene polymer, a vinylpyrrolidone homopolymer or copolymer, a polyalkoxylene glycol, a polysaccharide polymer or a mixture thereof.

14. A composition according to any of the preceding claims which further comprises at least another surfactant, a colorant, a bactericide, a thickener, a dye, a chelant, a pigment, a solvent, a stabilizer, a perfume, a corrosion inhibitor or a mixture thereof.

15. 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.

16. The use, in a liquid acidic composition, of a zwitterionic surfactant, to improve the greasy soap scum cleaning performance of said composition.

17. The use, in a liquid acidic composition of a zwitterionic surfactant, preferably a sulfobetaine surfactant, to reduce deposition of soap scum on a hard surface after said surface has been first treated with said composition.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 87 0058

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)
X	DATABASE WPI Section Ch, Week 9301 Derwent Publications Ltd., London, GB; Class D25, AN 93-004726 XP002042924 & JP 04 332 799 A (KAO CORP) , 19 November 1992 * abstract * ---	1-6,9, 14,15	C11D1/94
A	EP 0 666 304 A (PROCTER & GAMBLE) 9 August 1995 * the whole document * ---	1-12, 14-17	
A	US 5 061 393 A (LINARES CARLOS G ET AL) 29 October 1991 * claims * ---	1-12, 14-17	
A	WO 94 21772 A (PROCTER & GAMBLE) 29 September 1994 * the whole document * ---	1-12, 14-17	
A	DATABASE WPI Section Ch, Week 9050 Derwent Publications Ltd., London, GB; Class A97, AN 90-372270 XP002042925 & JP 02 269 200 A (KAO CORP) , 2 November 1990 * abstract * -----	1,2,14	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	8 October 1997	Grittern, A

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
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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