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(54) Use of polysaccharide polymer in liquid acidic composition

(57) The present invention relates to the use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, to treat a hard-surface, whereby after said hard-surface has first been treated with said composition, the formation of limescale deposits on said hard-surface when it comes in contact with water is reduced. Also the present invention relates to the use of a polysaccharide polymer or a mixture thereof in a liquid acidic composition to treat a hard-surface whereby improved shine/long lasting shine is delivered to the surface. Finally, the present invention also relates to the use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, for improved skin mildness

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Description

Technical field of the Invention

The present invention is related to acidic hard-surfaces compositions, especially limescale removal compositions.

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 water, resulting in an anaesthetic aspect of the 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.

It is also desirable that such liquid acidic compositions should have, in addition to the ability to effectively remove limescale deposits present on a surface, the ability to provide improved shine to the surface treated. It has now been observed that surface shine is often compromised by the low affinity the hard surface has with water when it comes in contact with it. Indeed, water has the tendency to form droplets on the surface rather than forming a thin film uniformly spread over the surface. This results as water evaporates in precipitation of poorly water soluble inorganic salts such as carbonate and/or phosphate salts with consequent formation of watermarks on the surface, and eventually limescale deposits, resulting in an anaesthetic aspect of the surface.

It is thus an object of the present invention to reduce formation of limescale deposits and/or of watermarks on a surface that has been treated with an acidic composition, especially an acidic limescale removal composition, and hence to provide improved shine to said surface.

The present invention overcomes these problems by the use of a polysaccharide polymer, in a liquid acidic composition suitable for descaling hard-surfaces. Indeed, it has been found that the addition of a polysaccharide polymer, preferably xanthan gum, in a liquid acidic composition, reduces or even prevents the formation of limescale deposits on a surface having first been treated with such a composition. Also less formation of watermarks are observed on a surface having been first treated with the compositions as described herein and then contacted with water, for example, during a rinse operation, thereby providing improved shine to said surface.

Advantageously, the shine benefit delivered to a hard surface treated with the compositions according to the present invention persists even after several cycles of rinsing thus providing long lasting protection against limescale redeposition/formation and/or watermarks formation on said surface, and hence long lasting shiny surfaces. In other words, the house wife will have the advantage to delay the next descaling operation.

Another advantage of the use of the polysaccharide polymer according to the present invention in a liquid acidic composition is that the surfaces treated become smoother (this can be perceived by touching said surfaces). This may also contribute to convey to consumers the perception of surface perfectly descaled.

The compositions described herein may be used on a variety of surfaces including metal surfaces such as aluminum, chromed steel, stainless steel, synthetic materials like vinyl, linoleum, glazed or non-glazed ceramic tiles, and/or enamel surfaces.

Background art

Limescale compositions comprising polysaccharide polymers like xanthan gum are known in the art. For example, EP-A-758 017 discloses acidic compositions with an acidic system and an acid-stable thickener, e.g. xanthan gum. EP-A-758 017 fails to disclose that polysaccharide polymers when added in a liquid acidic composition reduce the formation of watermarks and/or limescale deposits on a surface having been first treated with said composition, and thus provide improved shine to the surface.

Summary of the invention

The present invention encompasses the use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, to treat a hard-surface, whereby after said hard-surface has first been treated with said composition, the formation of limescale deposits on said hard-surface when it comes in contact with water is reduced.

The present invention further encompasses the use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, to treat a hard-surface whereby improved shine is delivered to the surface treated with said composition.

The present invention also encompasses the use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, to treat a hard-surface whereby long lasting shine is delivered to the surface treated with said composition.

Yet, the present invention also encompasses the use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, for improved skin mildness.

Detailed description of the invention

An essential feature of the present invention is a polysaccharide polymer or a mixture thereof.

Suitable polysaccharide polymers to be used 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 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®.

Xanthan gum or derivatives thereof are advantageously physically and chemically stable in the acidic conditions of the compositions herein, this even at very low pH typically below 1.5.

The acidic liquid compositions herein are chemically stable, i.e., there is virtually no chemical changes of the different ingredients due to reaction between different ingredients, and physically stable, i.e., that no phase separation occurs when stored in rapid aging test (RAT) at 50 °C for 10 days.

According to the present invention the compositions comprise from 0.001% to 10% by weight of the total composition of a polysaccharide polymer, or a mixture thereof, preferably from 0.01% to 3% by weight, more preferably from 0.01% to 1%, even more preferably from 0.05% to 0.8% and most preferably from 0.05% to 0.6%.

The polysaccharide polymers herein may act as a thickening agent, accordingly the liquid acidic compositions herein have a viscosity of from 1 cps to 1500 cps at 20°C, preferably from 20 cps to 800 cps and more preferably from 50 cps to 600 cps, when measured with a Carri-med rheometer CLS 100® at 5 N/m^2.

The liquid compositions according to 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 compositions according to the present invention are designed for removing limescale deposits. Thus, they typically comprise 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 according to 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 herein maleic acid is used alone as the acid of the acidic compositions according to the present invention.

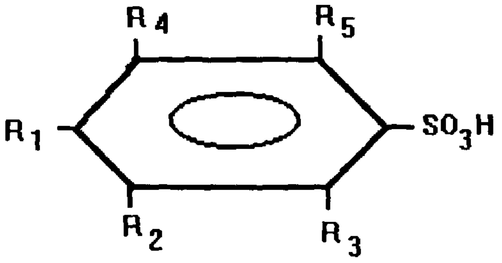
In another embodiment of the present invention, a second acid is added on top of said maleic acid. Said second acid is desired to strengthen the limescale removal performance. Preferably the second acids to be used herein which are particularly efficient to remove limescale on many surfaces, have their 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. Indeed, the addition of sulphamic acid to maleic acid-containing compositions improves the skin safety profile of said compositions. The skin will be less subject to become inflamed, red, sore and/or itchy when in contact with those acidic compositions according to the present invention comprising sulphamic acid on top of maleic acid, as compared to the same compositions without said sulphamic acid.

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 for use herein are those which comprise no or only one alkyl chain. 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 for use 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 according to 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%.

It has now surprisingly been found that the polysaccharide polymers described herein when added into a liquid acidic composition typically comprising an acid or a mixture thereof, preferably maleic acid and sulphamic acid, reduce the formation of limescale deposits and/or watermarks on a surface that has been first treated with said composition, when said surface comes into contact with water. This results in improved shine to the surface so treated when it comes into contact with both hard and/or soft water.

Although not wishing to be bound by theory, it has been observed that hard surfaces often have low affinity with water. This means that, when water gets in contact with hard-surfaces, its spreading, which is controlled by the interfacial energy (i.e., solid/liquid surface tension), is very limited. Indeed, it has been observed that the most stable configuration for the water is grouping in spherical droplets rather than forming a thin film uniformly spread over the surface. Then, as water droplets evaporate, their content of salt progressively become higher and higher so that poorly water soluble inorganic salts such as calcium/magnesium carbonate and/or phosphate salts eventually precipitate, i.e. form limescale deposits typically when water is hard and/or watermarks. The end result is a reduction of surface shine. It has now been found that when the polysaccharide polymers as described herein are added into a liquid acidic composition an hydrophilic layer is left on a hard-surface treated with said composition, said hydrophilic layer leaves the water coming in contact with the surface that has been first treated with said composition (e.g., water which is used to rinse off the surfaces having been so treated) uniformly spread over the surface ("sheeting effect") instead of forming droplets. This way, the formation of limescale deposits and/or watermarks upon drying is reduced or even prevented. This resulting in improved shine.

Furthermore, it has surprisingly been found that the polysaccharide polymers of the present invention have not only the ability to adhere on a surface treated with the acidic compositions herein comprising the same but to still remain adhered on the surface even after several cycles of rinsing (e.g., when water comes into contact with this surface later on, for example, during current household operation in a sink), thus providing long lasting protection against formation of limescale deposits/watermarks and, hence, long lasting shiny surfaces.

Not to be bound by theory, it is believed that the polysaccharide polymers also have the ability to form a film on the surface of the user skin, thereby providing improved skin mildness. In another embodiment the present invention thus also encompasses the use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, for improved skin mildness.

An additional advantage related to the use of the polysaccharide polymers of present invention is that, as they adhere on hard surface making them more hydrophilic, the surfaces themselves become smoother (this can be perceived by touching said surfaces) and this contribute to convey perception of surface perfectly descaled.

The liquid compositions according to the present invention are preferably aqueous compositions. Therefore, they 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%.

Optional ingredients

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

A highly preferred optional ingredient suitable to be used in the compositions according to the present invention is a surfactant or a mixture thereof. Surfactants are desired herein as they contribute to the cleaning benefits of the limescale removal compositions of the present invention. Indeed, the presence of a surfactant allows to boost the greasy soap scum cleaning of the compositions herein. More generally, the presence of a surfactant in the liquid acidic compositions according to the present invention allows to lower the surface tension and to improve the wettability of the surfaces being treated with the liquid acidic compositions of the present invention. The presence of a surfactant or a mixture thereof in the liquid acidic compositions according to the present invention helps to solubilize the soils.

Accordingly, the compositions herein may comprise a surfactant or a mixture thereof. The compositions according to the present invention may comprise up to 40% by weight of the total composition of said surfactant or a mixture thereof, more preferably from 0.05% to 15%, even more preferably from 0.1% to 10%, and most preferably from 0.1% to 5%. All types of surfactants may be used in the present invention including nonionic, anionic, cationic, zwitterionic or amphoteric surfactants. It is also possible to use mixtures of such surfactants without departing from the spirit of the present invention.

Highly preferred surfactants to be used herein are zwitterionic surfactants. Suitable zwitterionic surfactants for use herein contain both basic and acidic groups which form an inner salt giving 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 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, 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 is 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 ®.

Examples of particularly suitable sulfobetaine surfactants include tallow bis(hydroxyethyl) sulphobetaine, 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.

Example of amidobetaines 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".

Suitable amine oxides for use herein are according to the following formula R_1 R_2R_3NO wherein each of R1, R2 and R3 is independently a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups 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_1 R_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 groups 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_1 $R_2R_3R_4N^+X^-$, wherein X is a counteranion such as 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®.

Suitable nonionic surfactants for use in the compositions according to the present invention 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.

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).

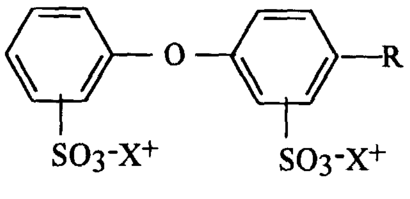
By "secondary C6-C20 alkyl or C6-C20 alkyl aryl sulphonates", it is meant herein that in the formula as defined above, the SO3M or aryl-SO3M group is linked to a carbon atom of the alkyl chain being placed between two other carbons of the said alkyl chain (secondary carbon atom).

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®.

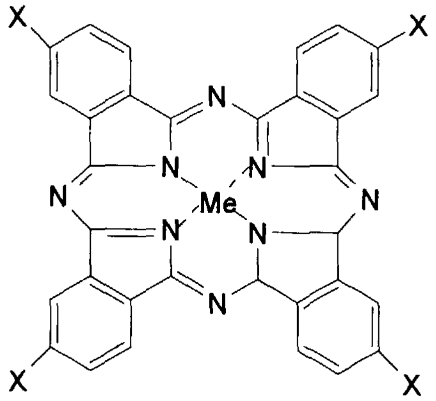
Other anionic surfactants useful herein include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product 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 for use 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.

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 according to the present invention may comprise up to 0.2% by weight of the total composition of a dye or a mixture thereof, preferably from 0.0001% to 0.015% and more preferably from 0.001% to 0.010%.

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. Indeed 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.

Limescale removal performance test method:

The limescale removal capacity of an acidic composition 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.

Shine test method:

Obtaining a good shine end result results from a good spreading of the liquid acidic composition over the surface when the surface is treated therewith and from the reduced formation of watermarks and even reduced precipitation of poorly water soluble salts that otherwise typically occurs in presence of hard water, when water evaporates. The ability of a composition to provide "shine" to the surface refers to the composition's ability to leave no watermarks after evaporation of water. This can be evaluated by human visual grading.

In a suitable test method two rectangular areas (10cmx4cm) of a sink (made of either stainless steel or ceramic) are treated with a composition according to the present invention and a reference composition, e.g. the same composition but without said polysaccharide polymer. 3 grams of composition is first poured onto each surfaces to be treated and, then wiped (10 strokes) by using a Spontex® sponge. Then each treated surface is rinsed with 200 grams of tap water and left to dry. After the surfaces treated with the compositions according to the present invention and those treated with the reference composition get dried, they are compared side by side and evaluated by visual grading to evaluate shine difference. Evaluation may be generally done by applying the Panel Score Unit (PSU).

In a long lasting shine test method the test method as mentioned above may be carried out, but the rinsing and drying cycle are repeated several times. Each time, after both the surfaces get dried they are compared side by side and evaluated by visual grading to see shine difference. Evaluation is generally done by applying the Panel Score Unit (PSU).

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	10	14	-	10	12
Sulphamic acid	2	2	-	2	-	2
Citric acid	-	-	-	2	2	2
Mirataine CBS®	2.0	2.0	-	2.0	-	2.0
HLAS	-	-	-	-	0.50	-
Xanthan Gum	0.2	0.1	0.1	0.3	0.4	0.5
Waters & Minors	up to 100					
Ingredients: (% by weight)	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**
Maleic acid	10	10	10	8	6	-
Sulphamic acid	2	2	2	-	-	2
Citric acid	-	1	-	2	4	8
Dobanol® 91.8	2	2	-	1	-	-
Mirataine CBS®	-	-	2	-	-	2.2
Xanthan Gum	-	-	0.05	-	0.50	0.1
Succinoglycan	0.05	0.1	-	0.05	0.05	-
Waters & Minors	up to 100					
Mirataine CBS® is cocoamidopropyl hydroxy sulphobetaine supplied by Rhone-Poulenc. HLAS is Linear alkyl benzene sulphonate in acid form. Dobanol® 91.8 is a nonionic surfactant supplied by Shell.						

All the compositions of the above examples exhibit excellent immediate and long lasting shine benefits on the surface treated while providing excellent limescale removal performance. Also good greasy soap scum cleaning performance have been obtained when these compositions are used to treat limescale-containing stains found in a kitchen and in a bathroom, this both when used neat or in diluted form.

Claims

1. The use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, to treat a hard-surface, whereby after said hard-surface has first been treated with said composition, the formation of limescale deposits on said hard-surface when it comes in contact with water is reduced.

2. The use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition to treat a hard-surface, whereby improved shine is delivered to the surface treated with said composition.

3. The use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition to treat a hard-surface, whereby long lasting shine is delivered to the surface treated with said composition.

4. The use of a polysaccharide polymer or a mixture thereof, in a liquid acidic composition, for improved skin mildness.

5. The use according to any of the preceding claims wherein said composition comprises from 0.001% to 10% by weight of the total composition of a polysaccharide polymer, or a mixture thereof, preferably from 0.01% to 3% by weight, more preferably from 0.05% to 0.8% and most preferably from 0.05% to 0.6%.

6. The use according to any of the preceding claims wherein said polysaccharide polymer is a substituted cellulose material or a naturally occurring polysaccharide polymer or a mixture thereof, preferably carboxymethylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, succinoglycan, xanthan gum, guar gum, locust bean gum, tragacanth gum or derivatives thereof, or mixtures thereof and more preferably xanthan gum or derivatives thereof or a mixture thereof.

7. The use according to any of the preceding claims wherein said composition comprises an organic or inorganic acid or a mixture thereof typically at a level of from 0.1% to 70% by weight of the total composition.

8. The use according to claim 7 wherein said acid is maleic acid alone or together with a second acid which has its first pKa not exceeding 5, or a mixture thereof.

9. The use according to claim 8 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.

10. The use according to claims 8 or 9 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%.

11. The use according to any of the preceding claims wherein said composition further comprises a surfactant or a mixture thereof up to a level of 40% by weight of the total composition, typically selected from the group consisting of anionic, nonionic, cationic, amphoteric, zwitterionic surfactants and mixtures thereof, more preferably at least a zwitterionic surfactant or a mixture thereof.

12. The use according to any of the preceding claims wherein said composition has a pH below 4, preferably a pH from 0.1 to 2.5 and more preferably from 0.1 to 2.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 87 0055

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)
A	EP 0 467 472 A (COLGATE PALMOLIVE CO) 22 January 1992 * page 5, line 4 - line 11; claims 1,17,19-22; examples * ---	1-12	C11D3/22
D,A	EP 0 758 017 A (PROCTER & GAMBLE) 12 February 1997 * the whole document * ---	1-12	
A	DATABASE WPI Section Ch, Week 9237 Derwent Publications Ltd., London, GB; Class A97, AN 92-304222 XP002042516 & JP 04 209 700 A (SANSHO KK) , 31 July 1992 * abstract * ---	1-12	
A	EP 0 303 188 A (HENKEL KGAA) 15 February 1989 * claims * ---	1-5,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP 0 342 997 A (UNILEVER) 23 November 1989 * claims * -----	1-5,11	C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	3 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
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