
Candidate's Answer

Removal of limescale deposits

Field of Invention

The present invention relates to compositions for the removal of limescale deposits from domestic and industrial appliances and apparatus.

Background to the Invention

Limescale deposits from water, which consist principally of magnesium and calcium carbonates, are not only unsightly but can also lead to the inefficient functioning of domestic appliances and apparatus such as for examples electric kettles, shower heads, taps, coffee makers and boilers, and also many industrial appliances and apparatus.

Compositions based on protonic acids such as citric, hydrochloric or sulphuric acids are known to be of use as descalers, i.e. as agents for the dissolution and removal of limescale. Strong acids, such as hydrochloric acid ($pK_a = -7$) and sulphuric acid ($pK_a = -3$) have the disadvantage that they are very corrosive. (The pK_a gives an indication of the acid strength; the lower the pK_a the stronger the acid. As usual, the pK_a values for acids with more than one acidic hydrogen atom refer to the abstraction of the first proton, e.g. for sulphuric acid (H_2SO_4) for the reaction $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$).

On the other hand, relatively weak acids, such as citric acid, exhibit a very slow and unsatisfactory dissolution of limescale ($CaCO_3/MgCO_3$), accompanied by the formation of cloudy solutions and by secondary precipitation of calcium salts. Moreover, only a part of the acid capacity of weak acids is utilized, making higher concentrations and larger amounts necessary.

Household and Personal Products, January 1984, discloses that the use of acetic acid for limescale removal is not recommended.

Acetic acid is not very effective when used at ambient temperature. If heated, acetic acid evaporates producing an irritant and unpleasant smelling vapour. And discloses that citric acid does not have these disadvantages. Aqueous solutions of citric acid are as effective limescale removing agents as acetic acid.

Described within this document is a limescale-removing agent, and it discloses that the *limescale-removing agent is usually prepared by dissolving citric acid in water. Concentrations of from 14 to 96 g/litre of citric acid are usually employed. These are the concentrations in which citric acid is normally used as a limescale removing agent in industrial appliances and apparatus.* This document also states that *citric acid may be replaced by the equivalent amount of tartaric acid if desired.*

However, nowhere in this document are the problems associated with the use of relatively weak acids such as citric and tartaric acid addressed.

Document 2, which was published on 24th September 1974, describes an *improved iron-tanned leather. This leather is tanned using a novel acidic composition containing a water-soluble salt of Fe³⁺ (i.e. of trivalent iron) and a protonic acid having an acid strength pK_a of 3 or more as essential ingredients. The protonic acids are preferably selected from di- or tricarboxylic acids, especially from citric acid and tartaric acid, with citric acid being especially preferred. Optionally, glycerine may be added. This solution is used substantially according to known tanning procedures. The novel leather obtained is characterised by a pleasant light-fast tan colour and an excellent shrink temperature.*

The solutions used in Document 2 *contain water, trivalent iron supplied in the form of ferric chloride (FeCl₃) and citric acid as the essential ingredients. The molar ratio of citric acid to FeCl₃ in Document 2 is preferably from 8:1 to 1:1, more preferably from 4:1 to 2:1.*

The object of the present invention is to provide a composition and method for the removal of limescale deposits *that provides a high rate of dissolution of the limescale, results in little corrosion and forms clear solutions unaccompanied by secondary precipitation, and that uses a solution that is easy to handle and safe to use.*

Summary of the Invention

The present invention provides a composition according to Claims 1 to 10 of the present application. Such compositions are very useful for the removal of limescale deposits, result in very little corrosion and do not suffer from the problem of secondary precipitation.

The present invention also relates to an aqueous solution according to Claim 11 of the present application.

The present invention further relates to a method of removal of limescale according to Claims 12 to 22 of the present application.

Finally, the present invention relates to the use of a composition as described in Claim 23 of the present application.

Detailed Description of the Invention

The compositions of the present invention *contain a medium strength to weak protonic acid (i.e. a protonic acid having an acid strength pK_a of 3 or more).* *The protonic acids employed in the present compositions are preferably di- or tricarboxylic acids. Examples of such acids are dicarboxylic acids such as tartaric acid and tricarboxylic acids such as citric acid, with citric acid being particularly preferred.*

Both citric and tartaric acids are crystalline and non-toxic. Both naturally occur in fruits (citric acid in citrus fruits, such as lemons; tartaric acid in grapes).

The compositions according to the present invention also contain a water-soluble salt of a trivalent cation of a metal or of a divalent cation of a transition metal.

Such salts are generally known and those mentioned below are commercially available. Preferred are the water-soluble salts of the divalent transition metal cations Cu^{2+} , Ni^{2+} and Zn^{2+} , and of the trivalent metal cations Fe^{3+} , Cr^{3+} and Al^{3+} . Water-soluble salts of divalent cations of metals which are not transition metals, e.g. salts of cations like Ca^{2+} and Mg^{2+} do not show any positive effect.

Preferred as anions of these salts are acetate, chloride and nitrate, with chloride being particularly preferred.

Examples of such salts are CuCl_2 , ZnCl_2 , CrCl_3 , FeCl_3 and AlCl_3 . If the present compositions are to be employed in domestic appliances, the water-soluble salts of Zn^{2+} and Fe^{3+} are preferred. They have the advantage of being less toxic.

Copper, chromium and aluminium salts are less preferred. Aluminium salts have been linked with Alzheimer's disease. Salts of copper and chromium are toxic.

If, however, the surface from which the limescale is to be removed is made of aluminium, it is essential to employ an aluminium salt as the water-soluble salt mentioned above. Otherwise, excessive corrosion of the aluminium surface will occur.

The molar ratio of the protonic acid to the water-soluble salts mentioned above is preferably from 8:1 to 1:1, more preferably from 4:1 to 2:1.

The compositions of the present invention are conveniently in the form of dry mixes or solutions, preferably concentrated solutions. Dry mixes may be in the form of powders, granules or tablets.

The compositions preferably also contain acid-base indicators. The preferred acid-base indicators are methyl orange and methyl red as they are stable even at elevated temperatures. Methyl orange and methyl red also do not stain plastic parts (like those used in many coffee makers).

These indicators are red in an acidic solution and yellow in a neutral or basic solution. If a composition of the present invention containing methyl red or methyl orange has turned yellow, this is an indication that it is no longer effective. The amount of acid-base indicator is not critical as long as its colour is clearly visible. Amounts of from 1 to 100 mg/l of the aqueous solution are usually sufficient.

It is most preferred if the compositions of the present invention are aqueous solutions of the compositions described above.

Preferably, the aqueous solution used contains from 0.075 to 0.5 moles/litre of the acid and from 0.03 to 0.3 moles/litre of the water-soluble salt. This corresponds to 14 to 96 g/litre of citric acid and to 4 to 41 g/litre of $ZnCl_2$ or 5 to 49 g/litre of $FeCl_3$. According to the present invention, limescale deposits may be dissolved by contacting the deposit with an aqueous solution of the composition as described above.

If the present composition is in the form of a dry mix then it is preferred to dissolve it in water before applying it to the limescale deposit. The time necessary for removing or dissolving limescale can be reduced considerably if the solution is treated with ultrasound whilst in contact with the limescale deposit.

This may be achieved, for example, by contacting the solution in the appliance or apparatus on which or in which the limescale deposit has been formed, with an ultrasound generator.

Also, contacting the limescale deposit with the aqueous solution of the composition described above at elevated temperatures may also be desirable to increase the efficiency of the method of removing the limescale deposit.

The method of the present invention is particularly suitable for the dissolution of limescale deposits on domestic appliances and apparatus including electric kettles, shower heads and taps.

CLAIMS

1. A composition comprising:
a protonic acid having an acid strength pK_a of 3 or more; and
a water-soluble salt of a trivalent cation of a metal or of a divalent cation of a transition metal, provided that the water-soluble salt of a trivalent cation is not a water-soluble salt of Fe^{3+} .
2. A composition according to Claim 1, wherein the protonic acid is a di- or tricarboxylic acid.
3. A composition according to Claim 1 or 2, wherein the protonic acid is tartaric acid or citric acid.
4. A composition according to any one of Claims 1 to 3, wherein the water-soluble salt is a salt of the divalent transition metal cations Cu^{2+} , Ni^{2+} or Zn^{2+} , or of the trivalent metal cations Cr^{3+} or Al^{3+} , or mixtures thereof.
5. A composition according to any one of Claims 1 to 4, wherein the anion of the water-soluble salt is selected from acetate, chloride or nitrate.
6. A composition according to any one of Claims 1 to 5, wherein the molar ratio of the protonic acid to the water-soluble salt is from 8:1 to 1:1.
7. A composition according to any one of Claims 1 to 6, wherein the composition is in the form of a dry mix or a solution.
8. A composition according to any one of Claims 1 to 7, wherein the composition additionally contains an acid-base indicator.

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9. A composition comprising:
a protonic acid having an acid strength pK_a of 3 or more;
a water-soluble salt of Fe^{3+} ; and an acid-base indicator.
 10. A composition according to Claim 8 or 9, wherein the acid-base indicator is methyl orange or methyl red.
 11. An aqueous solution comprising:
a protonic acid having an acid strength pK_a of 3 or more; and
a water-soluble salt of a trivalent cation of a metal or of a divalent cation of a transition metal, provided that the water-soluble salt is not $FeCl_3$.
 12. A method for removing limescale deposits from domestic and industrial appliances and apparatus comprising contacting the limescale deposit with an aqueous solution comprising:
a protonic acid having an acid strength pK_a of 3 or more; and
a water-soluble salt of a trivalent cation of a metal or of a divalent cation of a transition metal, with the proviso that if the limescale is removed from an aluminium surface, an aluminium salt is used.
 13. A method according to Claim 12, wherein the protonic acid is a di- or tricarboxylic acid.
 14. A method according to Claim 12 or 13, wherein the protonic acid is tartaric acid or citric acid.
 15. A method according to any one of Claims 12 to 14, wherein the water-soluble salt is a salt of the divalent transition metal cations Cu^{2+} , Ni^{2+} or Zn^{2+} , or of the trivalent metal cations Fe^{3+} , Cr^{3+} or Al^{3+} , or mixtures thereof.

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16. A method according to any one of Claims 12 to 15, wherein the anion of the water-soluble salt is selected from acetate, chloride or nitrate.
 17. A method according to any one of Claims 12 to 16, wherein the aqueous solution additionally comprises an acid-base indicator.
 18. A method according to any one of Claims 12 to 17, wherein the water-soluble salt is a Zn^{2+} or Fe^{3+} salt.
 19. A method according to any one of Claims 12 to 18, wherein the molar ratio of protonic acid to the water-soluble salt is from 8:1 to 1:1.
 20. A method according to any one of Claims 12 to 19, wherein the concentration of the acid in the aqueous solution is from 0.075 to 0.5 moles/litre and the concentration of the water-soluble salt is from 0.03 to 0.3 moles/litre.
 21. A method according to any one of Claims 12 to 20, wherein the solution is treated with ultrasound whilst in contact with the limescale deposit.
 22. A method according to any one of Claims 12 to 21, wherein the solution is at an elevated temperature whilst in contact with the limescale deposit.
 23. Use of a composition comprising:
 - a protonic acid having an acid strength pK_a of 3 or more; and
 - a water-soluble salt of a trivalent cation of a metal or of a divalent cation of a transition metal, for the removal of limescale deposits from domestic and industrial appliances and apparatus.