Candidate's Answer

The present invention concerns the removal of limescale deposits from surfaces and provides a method for limescale removal and compositions used in said method

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 applicances and apparatus such as for example electric kettles and shower heads.

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 $H_2SO_4=H^+ + HSO_4^-$).

Document 1 discloses the use of citric acid or tartaric acid in the removal of limescale deposits from domestic appliances.

However, such relatively weak acids *exhibit a very slow and unsatisfactory dissolution of limescale ($CaCO_3$/$MgCO_3$), accompanied by the formation of cloudy solutions and by the 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.*

Document 2, in the completely unrelated technical field of leather training, discloses a composition comprising citric or tartaric acid in combination with a water-soluble salt of Fe^{3+} (trivalent iron).

Document 1 (D1) is therefore the closest prior art to the present invention. The technical difference between the present invention and D1 is that the method provided by the present invention provides a high rate of dissolution of the limescale, results in little corrosion, forms clear solutions unaccompanied by secondary precipitation and uses a solution that is easy to handle and safe to use.

The objective technical problem solved by the present invention, therefore, is the provision of a more efficient method of removing limescale deposits.

Accordingly, there is provided a composition < insert claim 1 > . In a further embodiment of this aspect of the invention, there is provided a composition < insert claim 2 >. Preferably the indicator used is < insert claim 3 > 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 our invention containing methyl red or methyl orange has turned yellow, this is an indication that it is no longer effective.*

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 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.

The preferred water-soluble salts in the present invention are <insert claim 6>. *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 $CuCl_2$, $NiCl_2$, $ZnCl_2$, $CrCl_3$, ~~$FeCl_3$~~ *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.

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 aqueous (optionally *concentrated) solutions. Dry mixes may be in the form of powders, granules or tablets.*

Preferably, the aqueous solution used contains from 0.075 to 0.5 moles/litre of the acid and from m 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 $ZnCl_2$ ~~*5 to 49g 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.

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.*

In a further aspect of the present invention, there is therefore provided a method <insert claim 12>.

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.

In a yet further aspect of the present invention, there is provided the use of a composition <insert claim 14>.

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.

In a yet further aspect of the present invention, there is provided a method of preparation <insert claim 15> and a method of preparation <insert claim 16>.

The invention is described more fully by means of the following Examples.

Example 1

Dissolution of limescale.

40g of citric acid and 10 g of zinc chloride ($ZnCl_2$) were dissolved in water to produce a solution with a final weight of 1 kg.

Boiler limescale was broken into pieces measuring approximately 3x3x2 mm, and fines were removed by sieving.

A sample (250 ml) of the above-described solution was heated to 95°C and 15 g the prepared pieces of boiler limescale was added. The solution was allowed to cool and descaling was determined after 5 minutes. The residual scale was removed by filtering through a fine metal mesh. The residue was dried at 105°C for one hour. The dried residue was weighed. The percentage descale was then calculated from the difference between the initial weight and the residual weight of the limescale.

The percentage descale was determined analogously using times of 15 and 30 minutes respectively.

The results obtained were the following:

Time (minutes)	*Percentage descale*
5	*44*
15	*55*
30	*66*

<u>Example 2</u>

Corrosion Studies

A 1 kg solution of citric acid and zinc chloride was prepared according to example 1, poured into an electric kettle (New Haden Autojug Model AJ2) and left for 25 days. The solution was removed and inspection revealed no visible corrosion.

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 wherein the trivalent metal cation is not Fe^{3+}.

2. A composition comprising a protonic acid having an acid strength pKa of 3 or more; a water-soluble salt of a trivalent cation of a metal or of a divalent cation of a transition metal; and an acid-base indicator.

3. A composition according to claim 2 wherein the acid-base indicator is either methyl red or methyl orange.

4. A composition according to any of claims 1 to 3 wherein the protonic acids are di- or tricarboxylic acids.

5. A composition according to claim 4 wherein the protonic acid is citric acid.

6. A composition according to any preceding claim wherein the divalent transition metal cation is Cu^{2+}, Ni^{2+} or Zn^{2+} and the trivalent metal cation is Cr^{3+} or Al^{3+}.

7. A composition according to claim 6 wherein the water-soluble salt is $CuCl_2$, $NiCl_2$, $ZnCl_2$, $CrCl_3$ or $AlCl_3$.

8. A composition according to any preceding claim wherein the molar ratio of the protonic acid to the water-soluble salt is from 4:1 to 2:1.

9. A composition according to any of claims 1 to 8 which is in the form of a dry mix.

10. A composition according to any of claims 1 to 8 which is in the form of an aqueous solution.

11. A composition according to claim 10 which comprises from 0.075 to 0.[illegible] moles / litre of the protonic acid and from 0.03 to 0.3 moles / litre of the water-soluble salt.

12. A method of dissolving limescale deposits from surfaces which comprises contacting the deposit with an aqueous solution of a composition comprising a protonic acid having an acid strength pKa 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, wherein if the surface from which the limescale is to be removed is made of aluminium, the water-soluble salt is an aluminium salt.

13. A method according to claim 12 wherein the solution is treated with ultrasound whilst in contact with the limescale deposit.

14. The use of a composition comprising a protonic acid having an acid strength pKa 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 in the removal of limescale deposits from surfaces, wherein if the surface is made of aluminium, the water-soluble salt is an aluminium salt.

15. The preparation of a composition according to claim 9 comprising combining the protonic acid and the water-soluble salt together as solids to form a dry mix.

16. The preparation of a composition according to claim 10 comprising dissolving the protonic acid and the water-soluble salt together in water.

Notes to the Examiner

(1) Unity

In my opinion, claims 1 and 2 have unity according to Art 82 and Rule 29(2) as the claims relate to the same unified inventive concept, namely the combination of a protonic acid of pKa of >3 with a water-soluble metal (trivalent) or transition metal (divalent) salt.

(2) Disclaimer

The use of a disclaimer in claim 1 to disclaim a composition comprising trivalent iron (Fe^{3+}) is entirely allowable by the EPC in line with current case law (T1050/93) and the claim still has inventive step as the disclosure of D2 (for which the disclaimer in claim 1 provides novelty) is clearly in a completely different technical field (leather tanning) and addresses a totally different technical problem to that solved by the present invention.