

EUROPEAN QUALIFYING EXAMINATION 2006

PAPER A CHEMISTRY

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LETTER FROM THE APPLICANT

Lucius Limescale Ltd.
London

To
Pat & A. Gent

Dear Pat,

My company develops compositions for the removal of limescale deposits from domestic and industrial appliances and apparatus.

A published patent application and an article which was published several years ago are enclosed with this letter. I fear results of our research are covered by these documents. So we would like you to file a European patent application on our behalf as soon as possible. On the one hand this application should cover as much of our results as possible. On the other, such an application should also meet the requirements of novelty and inventive step and the other requirements of the European Patent Convention so that a patent might be granted without any further office action. Please note that I have invited our research department for a sailing trip on my yacht Lime Cloud II. We will leave tomorrow and we will not return before Christmas. No phones are allowed on board. So, you have to rely completely on the information given below when preparing the patent application. All the salts and acids, indicators, any other chemical compound mentioned, apparatus and devices described below are well known and commercially available.

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 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 ($\text{pK}_a = -7$) and sulphuric acid ($\text{pK}_a = -3$) 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 $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$).

On the other hand, relatively weak acids, such as citric acid, exhibit a very slow and unsatisfactory dissolution of limescale ($\text{CaCO}_3 / \text{MgCO}_3$), 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.

An object of our invention described below is to provide a method of dissolving limescale 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.

This object is attained by employing the aqueous solutions mentioned below.

These solutions 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 solutions according to our 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 concentrated solutions. Dry mixes may be in the form of powders, granules or tablets.

The compositions preferably 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 our 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.

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.

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 .

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.

Example 1

Dissolution of limescale

40 g 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 of 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

Example 2

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.

DOCUMENT 1

Household & Personal Products, January 1984

- 5 Limescale deposits from water can lead to the inefficient functioning of domestic appliances and apparatus such as electric kettles, coffee makers, taps, boilers and shower heads.

Several types of limescale-removing agent for domestic use are commercially available.

- 10 These are, however, rather expensive.

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.

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Citric acid does not have these disadvantages. Aqueous solutions of citric acid are as effective limescale removing agents as acetic acid. Pure citric acid is a solid. It is sold in the form of a powder, granules, tablets or concentrated solutions. A 375 g package of pure citric acid is sold for about 2.50 US \$.

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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.

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Citric acid may be replaced by the equivalent amount of tartaric acid if desired.

DOCUMENT 2

(published on 24 September 1974)

Leather

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The present invention concerns an improved iron-tanned leather. This leather is tanned using a novel acidic composition containing a water-soluble salt of Fe^{3+} (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.

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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.

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The Solutions

The solutions of this invention to be used for tanning preferably contain water, trivalent iron supplied in the form of ferric chloride (FeCl_3) and citric acid as the essential ingredients.

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The molar ratio of citric acid to FeCl_3 is preferably from 8:1 to 1:1, more preferably from 4:1 to 2:1.

Iron chloride (FeCl_3) is readily soluble in water.

Preferably, the aqueous solution used contains from 0.075 to 0.5 moles/litre of citric acid and from 0.03 to 0.3 moles/litre of FeCl_3 . This corresponds to 14 to 96 g/litre of citric acid
5 and 4.9 to 49 g/litre of iron chloride (FeCl_3). Up to 30 g/litre of glycerine may be added to obtain additional improvement.

The tanning solutions may be prepared from dry mixes or concentrated solutions of iron chloride (FeCl_3) and citric acid. Dry mixes may be in the form of powders, granules
10 or tablets.

Examples

The procedure involved placing fifteen grams of bated and pickled sheepskin in each of
15 two 400 ml beakers (Samples A and B) and covering each with one of the solutions as listed below. The skin was stirred in the solution and was allowed to stand overnight at room temperature. Sodium carbonate solution was then added slowly to each until the pH was raised to about 4.5 and remained at this value for ten minutes. The skin was removed, washed by hand and squeezed dry, treated with glycerine and then with
20 mineral oil and tacked to a drying board. After drying, Samples A and B were found pliable, and of a medium tan colour. Shrink tests were made and the results are shown below.

Treatment of Sample A

5	Solution:	FeCl ₃	10.5 g/litre
		Citric acid	26.3 g/litre
		Glycerine	21.0 g/litre

Shrink temperature: 200°F

10 Treatment of Sample B

15	Solution:	FeCl ₃	10.0 g/litre
		Citric acid	25.0 g/litre
		Glycerine	0 g/litre

Shrink temperature: 170°F

Claims:

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1. An acidic tanning solution containing water, iron chloride (FeCl₃) and a protonic acid having an acid strength pK_a of 3 or more.

2. A tanning solution according to claim 1 where the acid is citric acid or tartaric acid.

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3. A tanning solution according to claim 2 where the acid is citric acid.

4. A tanning solution of claim 1 which also contains glycerine.

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5. Leather tanned with the tanning solution of claim 1.