(54) Titre : AMELIORATIONS CONCERNANT DES COMPOSITIONS DE DETARTRAGE
(54) Title: IMPROVEMENTS RELATING TO LIMESCALE REMOVING COMPOSITIONS

(57) Abrégé/Abstract:
In limescale-removing compositions of pH 1-5, comprising 1-15 wt.% of a dicarboxylic acid and 1-30 wt.% of an anionic surfactant other than fatty acid, the presence of 0.1-10 wt.% of a fatty acid, prevents low temperature instability of the product which leads to precipitation of the dicarboxylic acid.
**Title:** IMPROVEMENTS RELATING TO LIMESCALE REMOVING COMPOSITIONS

**Abstract**

In limescale-removing compositions of pH 1-5, comprising 1-15 wt.% of a dicarboxylic acid and 1-30 wt.% of an anionic surfactant other than fatty acid, the presence of 0.1-10 wt.% of a fatty acid, prevents low temperature instability of the product which leads to precipitation of the dicarboxylic acid.
IMPROVEMENTS RELATING TO LIMESCALE REMOVING COMPOSITIONS

Technical Field

The present invention relates to compositions for the removal of limescale and/or other mineral deposits from hard surfaces.

Background to the Invention

Limescale mainly comprises calcium and magnesium carbonates, and can contain lesser amounts of soap scum, protein, particulates and other soils. Limescale is formed on evaporation of water containing said soils. While the deposit formed by evaporation is initially paste-like, it hardens with time to form a recalcitrant deposit.

Conventional cleaning compositions are generally buffered at alkaline pH so as to attack fatty soils. Limescale is resistant to the action of alkali and specialist cleaning compositions, of acid pH, are used to remove it.

It is known that the use of strong acids, such as hydrochloric acid will result in prompt removal of limescale but will also result in damage to surrounding surfaces, such as bath enamels, metals and certain polymers, where these are susceptible to attack by strong acids.

Limescale removing compositions of maleic acid in combination with nonionic surfactants, either in further combination with ionic detergents or with phosphoric acid
are known. In the absence of nonionic surfactants cleaning efficiency is greatly reduced. Maleic acid is known to be a particularly effective limescale remover and is less prone to attack surfaces than the inorganic acids. EP 0496188 (P&G) relates to compositions with 1-15% nonionic and 4-25% of maleic acid, having a pH of 1-4. Preferred compositions are formulated at pH 1-4 and comprise maleic and nonionic at specified levels but which are substantially free of both ionic detergents and phosphoric acid.

The use of other organic acids is known: GB-B-2149419 (Colgate-Palmolive: filed November 1983) relates to an acidic liquid cleaning composition of pH 3-5 which comprises a surfactant, water, a minor proportion of a non-sequestering acid which reacts with Ca and Mg soaps of higher fatty acids in soap scum (examples include glutaric acid) and a lesser minor proportion of an acid which forms a water insoluble calcium salt (phosphoric acid is given as an example), both acids being partially neutralised to a pH of 3-5.

EP-B-0411708 (Colgate-Palmolive: filed 31 July 1989) relates to an acidic (pH 1-4) aqueous cleaner for baths which are acid resistant or of zirconium white enamel which comprises surfactant, a C2-C10 organic acid other than oxalic and malonic acid, an aminoalkylene phosphonic acid and phosphoric acid.

EP-B-0040343 (BASF: filed 16 May 1980) is a granted European patent which relates to a composition comprising ethoxylated alcohol nonionic surfactant and C4-C8 aliphatic dicarboxylic acids or mixtures of such. The acids are present as 'colour stabilizers' and include a mixture of succinic, adipic and glutaric acids in the examples of the patent.
EP 0606712 (Clorox: published July 1994) relates to pH approx 2-3.5 cleaning formulations for the removal of mineral deposits which contain 3-10% in total of both a weak acid and its conjugate base at a molar ratio of 1:30 to 30:1 in which the weak acid has a pKa of 2-3.5. The compositions disclosed in this specification comprise citric acid (a tricarboxylic acid) and sodium citrate dihydrate as the limescale removing acids.

Despite the formulation work which had been done in this area it is believed that it is difficult to make formulations which are stable at low temperatures and/or which contain significant levels of succinic and adipic acids. This is especially true of concentrated systems which comprise around 8% of the dicarboxylic acid or acids when these compositions are shipped or stored at temperatures below 5 Celcius, where the precipitation of the acid is irreversible. Such temperatures may be encountered both during storage and shipping of a product prior to its commercial sale and while the product is being stored by the end user. While reversible precipitation may occur at lower acid levels this can still cause difficulties for the user who may not be aware that the precipitation has occurred (due to the opaque packaging which is used for these products) and may use the liquor above the precipitate without first warming the composition.

**Brief Description of the Invention**

We have now determined that limescale-removing compositions of pH 1-5, comprising:

a) a dicarboxylic acid,
b) a fatty acid and

c) an anionic surfactant other than fatty acid

are stable at lower temperatures than similar compositions which do not contain the fatty acid. It is believed that the fatty acid acts as a solubiliser for the dicarboxylic acids but the details of the mechanism are not fully understood.

Accordingly a first aspect of the present invention provides a limescale-removing composition of pH 1-5, comprising:

a) 1-15\%wt of a dicarboxylic acid,

b) 0.1-10\%wt of a fatty acid, and

c) 1-30\%wt of an anionic surfactant other than fatty acid

A second aspect of the present invention provides for the use, as a low temperature stabilising additive in a limescale removing composition comprising 1-15\%wt of a dicarboxylic acid and 1-30\%wt of an anionic surfactant other than fatty acid, of 0.1-10\%wt of a fatty acid.

**Detailed Description of the Invention**

In the following description all quantities are given in wt\% on product unless noted otherwise.
Dicarboxylic Acids:

Dicarboxylic acids suitable for use in the present invention include adipic, glutaric and succinic acid and mixtures thereof. The mixtures are preferred as these are commercially available. Typical mixtures which can be found in the marketplace comprise 30-35% adipic acid, 45-50% glutaric acid and 10-18% succinic acid. Such a mixture is available in the marketplace as Sokalan DCS (TM, ex. BASF). Another suitable mixture is available as Radimix (TM, ex. Radici). The use of essentially pure acids is not excluded but these have limited commercial availability and the mixed acids are preferred.

Typical levels of total dicarboxylic acid in the product range from 2-10%wt. Levels of 3-5% are preferred for dilute compositions and levels of 6-9% for concentrates.

Fatty Acids:

Fatty acids suitable for use in the compositions of the present invention include monocarboxylic acids with an average carbon chain length in the range C10-C18, preferably C12-C16.

C14 average chain length linear fatty acids (derivable from lauric acid oils such as coconut and palm-kernel fats) are particularly preferred. Longer chain length fatty acids are less soluble in the absence of expensive hydrotropes (such as alcohol and alkaryl sulphonates) or organic solvents. Suitable fatty acids are available in the marketplace as PRIFAC 7907 (TM ex. Unichema).

Typical levels of fatty acids range from 0.1-3%wt on product, with a range of 0.1-1%wt being particularly
preferred. Typical levels in dilute compositions are 0.25%wt with 0.5%wt being used in more concentrated products.

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**Surfactants:**

Preferably the anionic surfactant comprises one or more of the group comprising: primary and secondary alcohol sulphates, alcohol alkoxy sulphates, primary and secondary alkane sulphonates and alkyl aryl sulphonates.

The preferred anionic surfactants are the alcohol alkoxy sulphates, preferably the ether-sulphates. Most preferably C_{18}-C_{18} average chain length ether sulphates with an average of 0.5-3 moles of ethoxylation. Lauryl ether sulphate (1EO) is a suitable anionic surfactant for compositions of the invention.

20 Preferred levels of anionic surfactant range from 2-14%wt. Preferably 3-7%wt surfactant is present in dilute compositions and 8-12%wt is present in concentrated compositions.

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**Corrosion Inhibitors:**

Typically the compositions of the invention comprise one or more corrosion inhibitors. Phosphoric acid is a suitable corrosion inhibitor, and when present is conveniently employed at a level of 0.1-5%wt with levels of 0.5%wt being used in dilute product and 1%wt being used in concentrated products.
pH:

It is believed important that the pH of the composition is below the pKa of the fatty acid being employed. In general, the pKa of a C12-C16 fatty acid will be close to 4.9, consequently the pH of the compositions will generally be below this figure. Given that damage to surfaces can occur at pH's below 3.0 it is particularly preferred that the pH of the compositions of the invention falls into the range 3.0-4.5, with a pH of around 3.5 being typical. Sodium hydroxide or another suitable base is used to regulate the pH if required. Typical levels of base in the products of the invention are 0.1-1%wt.

Minors:

Preferred levels of perfume range from 0.1-2%wt. Acid stable perfumes are available from a variety of sources including the Quest company.

Various minor components may be present in the compositions of the present invention, these include opacifiers, colours, preservatives and fluorescers.

Typically, the present invention provides a limescale-removing compositions of pH 3.0-4.9, comprising:

a) 2-10%wt of one or more dicarboxylic acids selected from adipic acid, succinic acid and glutaric acid,

b) 0.1-3.0%wt of an (on average) C_{16}-C_{18} fatty acid,

c) 2-14%wt of C_{16}-C_{18} alcohol alkoxy sulphate with an average of 0.5-3 moles of ethoxylation,
d) 0-5% phosphoric acid,

e) 0-5% base

Preferred formulations for direct use comprise:

a) 3-5%wt of a mixture of adipic acid, succinic acid and glutaric acid,

b) 0.1-0.5%wt of an (on average) C_{12}-C_{14} fatty acid,

c) 3-7%wt of C_{10}-C_{18} ether sulphate (0.5-3 EO),

d) 0.1-5% phosphoric acid,

e) 0-5% base

Preferred concentrated formulations:

a) 6-9%wt of a mixture of adipic acid, succinic acid and glutaric acid,

b) 0.3-1.0%wt of an (on average) C_{12}-C_{14} fatty acid,

c) 8-13%wt of C_{10}-C_{18} ether sulphate (0.5-3 EO),

d) 0.1-5% phosphoric acid,

e) 0-5% base

The present invention will be further described with reference to the following non-limiting examples.
Examples

Materials used in the examples are identified as follows:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>LES 1EO</td>
</tr>
<tr>
<td></td>
<td>Lauryl ether sulphate with one mole of ethoxylation</td>
</tr>
<tr>
<td>Fatty Acid</td>
<td>PRIFAC 7907 (TM) ex. Unichema</td>
</tr>
<tr>
<td>Dicarb Acid</td>
<td>Radimix (TM) ex. Radici or Sokalan DCS (TM) ex. BASF or Succinic acid</td>
</tr>
<tr>
<td>10</td>
<td>Phos. Acid</td>
</tr>
<tr>
<td></td>
<td>Phosphoric Acid</td>
</tr>
<tr>
<td>Base</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>Preservative</td>
<td>PROXEL GXL(TM, ex ICI) (1,2-benzisothiazolin-3-one)</td>
</tr>
<tr>
<td>Perfume</td>
<td>GC 1550 A ex Quest</td>
</tr>
</tbody>
</table>

Compositions were prepared by mixing of the components. Compositions were prepared with proportions as given in Table 1 below, all components being given in wt% as 100%wt.

<table>
<thead>
<tr>
<th>Example</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>LES 1EO</td>
<td>5.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Fatty Acid</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>Dicarb Acid</td>
<td>4.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Phos. Acid</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Base</td>
<td>0.38</td>
<td>0.76</td>
</tr>
<tr>
<td>Preservative</td>
<td>0.016</td>
<td>0.032</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Water</td>
<td>to 100</td>
<td>to 100</td>
</tr>
</tbody>
</table>
Experiments were also performed with each of the dicarboxylic acids mentioned above in the absence of the fatty acid. It was determined that after storage at temperatures below 5°C: irreversible precipitation of the mixed dicarboxylic acids as crystals occurred when these were present at a concentration of 8%. In the diluted composition (4% mixed acids) the precipitation is reversible. Similar results were obtained with succinic acid alone: in this case, we have problems of irreversible precipitation were encountered at 0°C even with the diluted version (4.0% succinic acid).

For the compositions given in table 1 above no solubility problem was detected with both Sokalan DCS and Radimix and also with Succinic acid alone: while the product became slightly turbid at low temperatures precipitation of dicarboxylic acid crystals did not occur.
1. A limescale-removing composition of pH 1-5, comprising:
   a) 1-15%wt of a dicarboxylic acid.
   b) 0.1-10%wt of a fatty acid with an average carbon chain length of C10-C16, and
   c) 1-30%wt of an anionic surfactant other than fatty acid
   and which is free of organic solvents.

2. Composition according to claim 1 wherein the dicarboxylic acid comprises one or more of adipic, glutaric, succinic acid and mixtures thereof.

3. Composition according to claim 1 or 2 wherein the anionic surfactant comprises one or more of the group comprising: primary and secondary alcohol sulphates, alcohol alkoxy sulphates, primary and secondary alkane sulphonates and alkyl aryl sulphonates.
4. A limescale-removing composition of pH 3.0-4.9, comprising:

a) 2-10%wt of one or more dicarboxylic acids selected from adipic acid, succinic acid and glutaric acid,

b) 0.1-3.0%wt of an (on average) C₁₀-C₁₆ fatty acid,

c) 2-14%wt of C₁₀-C₁₈ alcohol alkoxy sulphate with an average of 0.5-3 moles of ethoxylation,

d) 0-5% phosphoric acid,

e) 0-5% base

and which is free of organic solvents.