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<p>(21) International Application Number: PCT/GB91/01372 (22) International Filing Date: 12 August 1991 (12.08.91) (30) Priority data: 9110066.9 9 May 1991 (09.05.91) GB (71) Applicant (for all designated States except US): CUSSONS (INTERNATIONAL) LIMITED [GB/GB]; Bridgewater House, 60 Whitworth Street, Manchester M1 6LU (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : TRANTER, Inderhir [GB/GB]; 60 Havisham Close, Warrington, Cheshire WA3 7BD (GB). TIDESWELL, Philip, Ian [GB/GB]; 8 Brentwood Avenue, Urmston, Manchester M31 1XP (GB).</p>		<p>(74) Agents: LOW, Peter, John et al.; Wilson, Gunn & Ellis, 41 Royal Exchange, Manchester M2 7BD (GB). (81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i></p>
<p>(54) Title: LIMESCALE REMOVER</p>		
<p>(57) Abstract</p> <p>Known compositions for removing limescale do not remain in contact with the scale on non-horizontal surfaces for a sufficient time to be effective. The invention provides a limescale remover composition comprising an acid, a desolubiliser and a cationic surfactant. The cationic surfactant increases the viscosity so that the composition does not readily run off non-horizontal surfaces.</p>		

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LIMESCALE REMOVER

This invention relates to a composition for removing deposits of scale and the like.

Water hardness is a condition which results when rainwater percolates through rock formations such as limestone or chalk and dissolves inorganic salts, particularly calcium carbonate. Water which contains more than about 100 parts per million of calcium carbonate is usually considered as hard. When hard water evaporates the dissolved calcium carbonate is deposited on the adjacent surface in the form of tiny crystals. This is known as limescale. With time these limescale deposits can build up into quite a large size. Limescale is strongly bonded to the surfaces on which it is deposited and is difficult to remove. Well known examples of limescale deposits are the encrustations around the nozzles of taps, shower heads and around plugholes, the staining of the surfaces of baths, basins and sinks below the taps and the general dulling of the surfaces of such vessels that receive hard water. Limescale deposits can also occur when hard water is heated an example of this being the well known furring of kettles. Deposits can also be formed in washing machines and dishwashing machines.

Limescale removers have been developed in order to deal with these problems. These are generally based on

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acid which will react with the deposited scale to form a salt which is more readily soluble in water than calcium carbonate and which can thus be washed away. There are two main types of limescale remover. One type includes a strong acid (e.g. hydrochloric acid, sulphamic acid) so that the pH of the limescale remover composition is about 1.0 or less. As a result of this low pH such compositions have a thin, watery consistency since stable thickening systems have not been previously achievable. Although this type of limescale remover is quite effective it is difficult if not impossible to maintain contact between the limescale remover composition and limescale when the surface being treated is inclined to the horizontal. The other type of limescale remover includes a weak acid, (e.g. citric acid, acetic acid) resulting in a composition having a pH usually in the range of from 3 to 5. With such mild pH conditions such compositions can be easily thickened. While these compositions may remain in contact with a non-horizontal surface to be treated for a longer time than the strong acid type of composition, they have a poor performance. Hence they must remain in contact with the surface being treated for a considerable time for example up to half an hour. Even quite viscous compositions cannot with certainty be expected to remain in contact for that length of time with non-horizontal surfaces, particularly vertical surfaces such as the sides of a bath or on a tap.

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The present invention has been made in order to deal with this problem.

According to the invention there is provided a composition for effectively removing deposits of scale and the like from horizontal and inclined surfaces, said composition comprising an acid, a cationic surfactant and a desolubiliser.

It has been discovered that the combination of cationic surfactant and desolubiliser acts as a thickener providing increased viscosity for example up to 800 cps (Brookfield RV3/25°). Compositions having a viscosity of this order will tend to "cling" to vertical and non-horizontal surfaces thus giving the necessary contact time for effective scale removal.

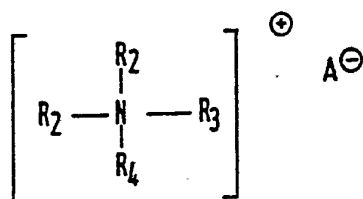
The acid used in the composition may be one which is used in conventional limescale removers, such as mineral acids, e.g. sulphamic acids, hydrochloric acids, phosphoric and organic acids, e.g. acetic acid, hydroxyacetic, citric acid, lactic acid.

The preferred cationic surfactants are di (higher alkyl) quaternary ammonium compounds (where higher alkyl means alkyl groups having from 8 to 30 carbons preferably from 11 to 22 carbons). Particularly

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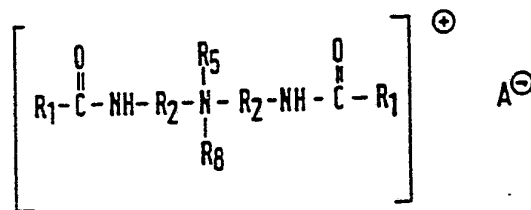
preferred quaternary ammonium compounds are the following:-

(i) acyclic quaternary ammonium salts having the formula:-



wherein R_2 is an acyclic aliphatic C_{15} - C_{22} hydrocarbon group. R_3 is a C_1 - C_4 saturated alkyl or hydroxyalkyl group, R_4 is selected from R_2 and R_3 and A is an anion.

(ii) diamido quaternary ammonium salts having the formula:-

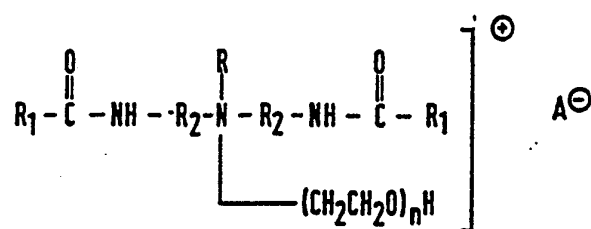


wherein R_1 is an acyclic aliphatic C_{15} - C_{21} hydrocarbon

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group, R_2 is a divalent alkylene group having 1 to 3 carbon atoms, R_5 and R_8 are C_1 - C_4 saturated alkyl or hydroxyalkyl groups and A is an anion:-

(iii) diamido alkoxyated quaternary ammonium salts having the formula:-



wherein n is equal to 1 to about 5, R_1 , R_2 , R_5 and A^- are as defined above;

(iv) quaternary imidazolinium compounds.

Examples of Component (i) include dialkyldimethylammonium salts such as ditallowdimethylammonium chloride, ditallowdimethylammonium methylsulfate, di(hydrogenated tallow) dimethylammonium chloride, distearyldimethylammonium chloride, dibehendyldimethylammonium chloride.

Examples of component (ii) include methylbis(tallowamidoethyl) (2-hydroxyethyl) ammonium

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methylsulfate and methylbis(hydrogenated tallowamidoethyl) (2-hydroxyethyl) ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl) (2-hydroxyethyl) ammonium methylsulfate wherein R_1 is an acyclic aliphatic $C_{15}-C_{17}$ hydrocarbon group. R_2 is an ethylene group, R_5 is a methyl group, R_8 is a hydroxyalkyl group and A is a methylsulfate anion; these materials are available from Sherex Chemical Company under the trade names Varisoft (R) 222 and Varisoft (R) 110, respectively.

Examples of (iv) include

1-methyl-1-tallowamido-ethyl-2-tallowimidazolinium methylsulfate and 1-methyl-1(hydrogenated tallowamidoethyl)-methylsulfate.

The quaternary ammonium salt (b) preferably comprises from 1% to 20%, more preferably 2% to 20% by weight of the composition herein.

The weight ratio amine (a): quaternary ammonium salt (b) is in the range from 10:1 to 1:10, preferably from 3:1 to 1:3.

The di(higher alkyl)imidazolinium compounds are preferred for use in the invention, in particular the 1-(lower alkyl)-1-(higher alkyl)amidoethyl-2-(higher alkyl) imidazolinium compounds, where "lower alkyl"

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means alkyl having from 1 to 4 carbon atoms, and "higher alkyl" means alkyl having from 11 to 22 carbon atoms.

The preferred desolubilisers are for example sodium xylene sulphonate and sodium cumene sulphonate.

The amounts of cationic surfactant and desolubiliser used are chosen having regard to the desired viscosity of the composition. However, amounts in the range 50.0 to 1.0% and 0.0 to 50% (by volume) respectively are preferred.

The composition of the invention may include the usual additives such as perfume, colourant and the like.

The following Example further illustrates the invention:-

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EXAMPLE

A limescale remover composition was formulated as follows:-

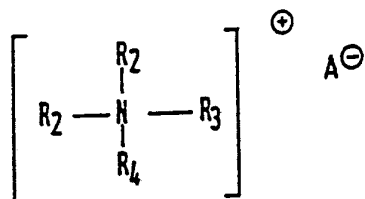
	<u>% by volume</u>
Sulphamic acid	12.5
Cationic surfactant ("Arquad" 18-50)	6.0
Sodium xylene sulphonate (SXS-40)	4.0
Perfume	0.5
Ink Blue R	0.002
Water	to 100.00

The composition had a viscosity of 200 cps (Brookfield, RV 3 @ 25°C) compared to the viscosity of 10 cps of a known composition having the same formulation as above, but without the cationic surfactant and sodium xylene sulphonate and including 3.0% of emulsifier.

CLAIMS

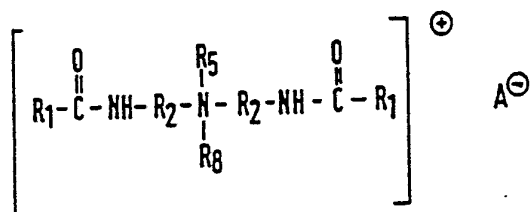
1. A composition for effectively removing deposits of scale and the like from horizontal and inclined surfaces, said composition comprising an acid, a cationic surfactant and a desolubiliser.
2. A composition as claimed in Claim 1, wherein the acid is a mineral acid such as sulphamic acid, hydrochloric acid or an organic acid such as acetic acid, hydroxy acetic acid and citric acid.
3. A composition as claimed in Claim 1 or Claim 2, wherein the cationic surfactant is a quaternary ammonium compound.
4. A composition as claimed in Claim 3, wherein the cationic surfactant is a di(higher alkyl) quaternary ammonium compound where higher alkyl is an alkyl group having from 8 to 30 carbon atoms.
5. A composition as claimed in Claim 4, wherein the quaternary ammonium salt is an acyclic quaternary ammonium salt having the formula

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wherein R_2 is an acyclic aliphatic C_{15} - C_{22} hydrocarbon group. R_3 is a C_1 - C_4 saturated alkyl or hydroxyalkyl group, R_4 is selected from R_2 and R_3 , and A is an anion.

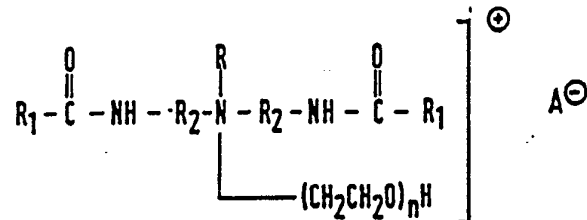
a diamido quaternary ammonium salt having the formula:



wherein R_1 is an acyclic aliphatic C_{15} - C_{21} hydrocarbon group. R_2 is a divalent alkylene group having 1 to 3 carbon atoms, R_5 and R_8 are C_1 - C_4 saturated alkyl or hydroxyalkyl groups and is an anion:

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a diamido alkoxyated quaternary ammonium salt having the formula:



wherein n is equal to 1 to about 5, and R₁, R₂, R₅ and A⁻ are as defined above; or a quaternary imidazolinium compound.

6. A composition as claimed in any preceding claim, wherein the desolubiliser is sodium xylene sulphonate or sodium cumene sulphonate.

7. A composition as claimed in any preceding claim wherein the cationic surfactant and the desolubiliser are present in the proportions of from 15.0 to 1.0% and 1.0 to 15.0% by volume respectively.

INTERNATIONAL SEARCH REPORT

PCT/GB 91/01372

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C02F5/08; C02F5/12; C02F5/10		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C02F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 157 552 (CALGON CORPOR.) 9 October 1985 see page 11; claims 1-3 ---	1-3
A	US,A,4 435 303 (KHODABANDEH,A.) 6 March 1984 see column 2, line 62 - column 3, line 10 see column 4, line 48 - line 54 ---	1,2
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>⁹ Special categories of cited documents :¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
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International Searching Authority	Signature of Authorized Officer	
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 9101372
SA 50485**

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		AU-B- 575384	28-07-88
		AU-A- 4032085	03-10-85
		CA-A- 1233000	16-02-88
		JP-A- 60220197	02-11-85

US-A-4435303	06-03-84	None	
