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(54) Title: HARD SURFACE CLEANERS FOR IMPROVED SHINE

(57) Abstract

The use of magnesium ions is disclosed in hard surface cleaning compositions comprising an anionic surfactant system, whereby the residuality of said compositions on said surfaces is reduced while cleaning performance is maintained. The compositions according to the present invention are designed to allow for in situ complexation of magnesium ions which are present in water, either during manufacture, or upon use.

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# Hard Surface Cleaners for Improved Shine

## Technical Field

The present invention relates to the cleaning of hard surfaces, especially glossy surfaces.

## Background

Compositions for the cleaning of hard surfaces are extensively discussed in the art. It is desirable that such compositions should have, in particular, the ability to provide a good shine to the cleaned surfaces. However, surface shine is often compromised by residues of the compositions which are left on said surfaces and which appear as streaks as water evaporation is completed.

This streaking phenomenon caused by a composition's residuality tends to be more of a problem as said composition is formulated as a concentrate, i.e it comprises more actives and less water.

Also, for a given composition, the residuality of said composition is even more noticeable as said composition is used to clean surfaces made of glossy materials, such as glossy ceramic tiles, windows and mirrors, or such materials as polyurethane-coated PVC which is widely used in Northern America.

Also, many products of today are formulated or can be used as no-rinse products. This residuality problem tends to be more acute for such products or in such conditions, as the rinsing step performed for other products cannot participate here to decreasing the residuality.

It is thus an object of the present invention to provide improved shine to hard surfaces, in a manner which is applicable to a variety of cleaning compositions, and a variety of surfaces.

Various solutions have been proposed in the art to meet this object, including the use of certain solvents, or the formulation of specific ingredient combinations.

In co-pending application EP-A-93202452.4, we disclosed the finding that this object could be met by formulating a composition which comprises an anionic surfactant system and an effective amount of magnesium ions as counterions for said anionic surfactants. In other words, for any given cleaning composition comprising an anionic surfactant system, which causes residues to appear on cleaned surfaces, adding an appropriate amount of magnesium ions will cause said residues to appear less, or even not to appear anymore.

Cleaning compositions comprising magnesium ions had been extensively described in the art, mainly in the context of dish washing, for instance in WO-A-9 206 171, WO-A-9 206 156, US-A-4 129 515, GB-A-2 078 246, EP-A-0 107 946, EP-A-0 062 371, FR-A-2 324 723, FR-A-2 296 688, EP 125 711, GB 2 144 763, and GB 2 078 246, but the benefits derivable therefrom in terms of low residuality had never been acknowledged.

However, the technology disclosed in the '452 application has certain drawbacks. A first drawback is that it requires the specific addition of magnesium for this unique purpose. Indeed, adding magnesium to the finished product for this only purpose is economically unattractive. As an alternative, one could use anionic surfactants neutralized with magnesium ions, but this is also more expensive than using the traditional sodium salts of anionic surfactants. Another drawback is that when the product is to be formulated at higher pH, typically 9 and above, adding magnesium salts would inevitably lead to formation and precipitation of magnesium hydroxide in the finished product.

We have now found that the shine benefits derivable from magnesium ions could be obtained, without adding any magnesium, in any form, in the compositions. We have found that the magnesium ions which are naturally present in tap water could be used to provide this benefit, by formulating compositions with which the magnesium ions would be complexed in situ, upon contact with water. We have found that the compositions according to the present invention are especially convenient for usage in neat and dilute usage. Indeed, shine benefits have also been observed in neat usage (i.e. when the composition is not diluted prior to usage). In this neat usage mode, the composition needs to be rinsed off of the cleaned surface, and we speculate that it is upon rinsing that the magnesium complexation occurs. In dilute usage, the complexation occurs. Thus the compositions herein are especially suitable for use neat or dilute.

Compositions herein are preferably used in dilute form, but they also perform well in undiluted, i.e. neat form, which is typically required for tougher soils such as cooker tops. We have also found that the neat grease cleaning performance of the compositions herein is unaffected by dilution in the concentration range herein.

## Summary of the Invention

The present invention encompasses hard surface cleaning compositions which comprise an anionic surfactant, which complexe magnesium ions as said compositions are concentrated with water comprising magnesium ions.

The present invention further encompasses concentrated and diluted aqueous compositions comprising a short chain anionic surfactant, a long chain anionic surfactant, and a hydrotrope, in selected ratios.

The present invention further encompasses methods of using said composition.

## Detailed Description of the Invention

The compositions of the present invention improve the shine on surfaces on which they are applied, in that they reduce the residuality of cleaning compositions for hard surfaces.

As used herein, the word "residuality" refers to the propensity of a composition to leave visible residues on a given surface. A composition with a high residuality is a composition which leaves substantially visible residues on surfaces, and which is therefore improper for use in a no-rinse mode. A composition's residuality in given usage conditions can be evaluated by measuring the glossiness of a surface cleaned with said composition, for instance using a glossmeter, or visually by a panel of expert judges.

The present invention is based on the finding that, in compositions comprising an anionic surfactant system, using magnesium ions as counterions for said anionic surfactant system will reduce the residuality of said compositions. This residuality reduction phenomenon, i.e. the reduction of the visibility of residues, but not necessarily the amount of residues, is clearly noticeable by eye, and it can be quantified by measuring the glossiness of a given surface cleaned with a composition of the present invention.

In the hard surface cleaning compositions according to the present invention, the magnesium ions are complexed in situ, as a composition according to the present invention is contacted with water comprising magnesium ions, either prior to usage, or upon rinsing after usage.

We have found that in a preferred enbodiment herein, there are three essential constituents required to achieve in situ complexation of magnesium, while ensuring good neat grease cleaning performance: they are a short chain anionic surfactant, a long chain anionic surfactant, and a hydrotrope, in specific proportions. All % herein are % by weight of the total composition, unless otherwise specified.

Accordingly, the compositions of the present invention are aqueous compositions, which comprise from 40% to 97% water, preferably from 50% to 95%. It is highly preferable to use demineralized water to manufacture the compositions herein, in order to avoid the issues generally associated with the use of "tap water" at the manufacturing stage, typically precipitations of various materials depending on the formulation parameters. If tap water is nevertheless used during manufacture, said water is generally sufficient to provide the magnesium ions which are complexed in situ - in this case - during manufacture.

The compositions of the present invention comprise a short chain anionic surfactant and a long chain anionic surfactant. Suitable anionic surfactants for use herein include those well known in the art, i.e. alkyl sulfates, alkyl ether sulfates, alkyl sulfonates, alkyl benzene sulfonates, alkyl succinates, alkyl carboxylates, alkyl ether carboxylates, alkyl sarcosinates, alkyl sulfo succinates and the like.

As used herein, the term "short chain anionic surfactant" refers to a surfactant as described above, where the alkyl chain has from 6 to 10 carbon atoms, or mixtures thereof. Preferred short chain anionic surfactants for use herein are those where the alkyl chain has 8 carbon atoms, as well as mixtures of two short chain anionic surfactants where one has 7 carbon atoms and the other has 9 carbon atoms. Also, we have found that it is preferred that the short chain surfactants be of the sulfate type, as opposed to sulfonate, preferably an alkyl sulfate. Short chain anionic surfactants are commercially available for instance from Rhone Poulenc under the trade name Rhodapon ®, or from Witco under the trade name Witconate ®.

As used herein, the term "long chain anionic surfactant" refers to a surfactant as described above, where the alkyl chain has from 10 to 20 carbon atoms, or mixtures thereof. Of course, if the short chain above has 10 carbon atoms, then the long chain should have more than 10 carbon atoms. Preferred long chain anionic surfactants for use herein are those where the alkyl chain has from 12 to 16 carbon atoms. Also, we have found that it is preferred that the long chain surfactants herein be of the sulfonate type, as opposed to sulfate, preferably an alkyl sulfonate, most preferably a secondary sulfonate. Suitable long chain anionic surfactants are commercially available from Hoechst under the trade name Hostapur ®, or from Hüls under the trade name MARLON ®.

Both anionic surfactants can conveniently be provided to the composition in the form of neutralized salts, with any conventional, commercially available counterion, typically Na, K, Li, NH4 or alkanolamine. As discussed in the background herein, it is a benefit of the present invention that it allows not to use magnesium salts of anionic surfactants, which are expensive to make. From this economical point of view, it is highly preferred to use sodium salts of anionic surfactants. Short chain anionic surfactants and long chain anionic surfactants herein can be provided with identical or different counterions.

According to the present invention, it is essential that the long chain surfactant and the short chain surfactant be present in a defined ratio range, namely from 1:0.1 to 1:4 (long chain to short chain), preferably from 1:0.5 to 1:2. also the compositions herein typically comprise from 0.2% to 8% of said short chain anionic surfactant, preferably from 0.5% to 4%, and from 0.5% to 10% of said long chain anionic surfactant, preferably from 2% to 5%.

The compositions herein may further comprise additional surfactants, including nonionic surfactants, typically alkyl alkoxylates, and zwitterionic surfactants, preferably nonionic surfactants.

As another essential ingredient, the compositions herein should comprise a hydrophope. Suitable hydrophopes for use herein include $C_1$-$C_4$ alkyl benzene sulfonates, branched or linear.

Suitable hydrotropes for use herein are commercially available from Hüls under the trade name Na Cumol Sulfonat ®, or from Manro under the trade name SCS 40 ®. Preferred for use herein are cumene sulfonates and xylene sulfonates, preferably their sodium salts. The compositions herein may comprise from 0.5% to 5% of said hydrotrope, preferably from 1% to 4%. But it is essential that the hydrotrope be present in a certain ratio range to said short chain anionic surfactant, namely 0.05:1 to 40:1, more preferred 0.25:1 to 4:1.

The compositions herein can be formulated in a variety of pH range, above the anionic surfactants' pKs, otherwise said anionic surfactants become protonated, and cannot effectively complex magnesium anymore. Also, as discussed in the background herein, the present invention is particularly useful for compositions formulated at pH above about 9, in which magnesium sulfate would precipitate as magnesium hydroxide if it was simply added on top in finished product. Thus the compositions herein are formulated at a pH of 9 or more, preferably of from 9 to 12, preferably 10 to 11.

The compositions herein may further comprise a variety of other ingredients, including, builders such as carbonates, citrates, alkanolamines, solvents, bleaches, enzymes, dyes, perfumes and other aesthetics.

The present invention further encompasses methods of using the compositions herein. In a first method, generally referred to as a "dilute usage", a composition according to the present invention is diluted in water, whereby magnesium ions from the dilution water are complexed in situ, before it is applied onto a hard surface. In a second method, generally referred to as a "neat usage", a composition according to the present invention is applied onto a hard surface without having been diluted, and subsequently rinsed off of said surface with water, whereby magnesium ions from the rinse water are complexed in situ.

Another, less preferred method herein is a method of manufacturing a composition according to the present invention, where the ingredients constituting the composition are mixed with water, i.e. the "processing water", containing magnesium ions, whereby the magnesium water from the processing water are complexed in situ. As briefly explained hereinbefore, this method requires the use of tap water as opposed to demineralized water. This method allows in situ complexation of magnesium, but in some instances it may lead to precipitation phenomenons.

The present invention is further illustrated by the following examples.

Examples-Experiments

The following compositions were made by mixing the listed ingredients in the listed proportions. Then, they were diluted and used to clean various tiles. The experiment was performed with distilled water (no magnesium), soft water (3gpg) and hard water (20 gpg). The shine, i.e. the residuality was evaluated visually and graded by a panel of 4 expert judges, using 3 replicates per composition and per dilution condition. The results are expressed as panel score units (psu) ref. from 1 to 4 as shine improves.

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| NaParaffin sulfonate | 3 | 3 | 1.5 | 1.5 | 4 | 2 |
| C8 Alkyl sulfate | 2 | 2 | 1 | 1 | 2 | 1.5 |
| C7-11(EO)6 | 8 | 10 | 4 | 5 | 6 | - |
| C13-15 (EO)30 | 5 | 4 | 2.5 | 2 | - | - |
| C12-13 (EO)3 | 3 | 4 | 1.5 | 2 | - | - |
| Palm kernel fatty acid | 0.5 | 0.5 | 0.2 | 0.2 | - | - |
| Na Cumene sulfonate | 3 | 3 | 1.5 | 1.5 | 2 | - |
| Na Xylene sulfonate | - | - | - | - | - | 2 |
| K2CO3 | 2 | 2 | 1 | 1 | - | - |
| MEA | - | - | - | - | 2 | 1.5 |
| pH | 10.5 | 10.5 | 10.5 | 10.5 | 11 | 11 |
| water/minors | ----------balance---------- | | | | | |

Results:

| | 1 psu ref. | 2 psu ref. | 3 psu ref. | 4 psu ref. |
|---|---|---|---|---|
| Distilled water | | | | |
| Soft water (3gpg) | +1 | +1.2 | +1.2 | +1.0 |
| Hard water (20 gpg) | +2 | +2.2 | +2.0 | +2.5 |

These results demonstrate that the shine benefit is obtained only when the dilution water contains magnesium, and the shine improves as the water hardness increases.

Claims

1. A hard surface cleaning composition which comprises an anionic surfactant, which complexes magnesium ions as said composition is contacted with water comprising magnesium ions.

2. A composition according to claim 1 which is aqueous, has a pH of above 9, comprises a short chain anionic surfactant comprising a C6-10 alkyl chain, a long chain anionic surfactant comprising a C10-20 alkyl chain and a hydrotrope, in weight ratios of said long chain anionic surfactant to said short chain anionic surfactants of from 1:0.1 to 1:4 and of said short chain anionic surfactant to said hydrotrope of from 1:0.05 to 1:4.

3. A composition according to claim 2 wherein said ratios are, respectively, 1:0.5 to 1: 2 and 1:0.25 to 1:4.

4. A composition according to claims 2 and 3 which comprises from 0.2% to 8% of said short chain anionic surfactant comprising a C6-10 alkyl chain, preferably from 0.5% to 4%.

5. A composition according to claims 2-4 comprising from 0.5% to 10% of said long chain anionic surfactant comprising a C10-20 alkyl chain, preferably from 2% to 5%.

6 A composition according to claims 2-5 which comprises from 0.5% to 5% of said hydrotrope, preferably from 1% to 4%.

7. A composition according to claims 2-6 wherein said short chain anionic surfactant is a C6-10 alkyl sulfate.

8. A composition according to claims 2-7 wherein said long chain anionic surfactant is a C10-20 alkyl sulfonate.

9. A composition according to claims 2-8 which comprises from 40% to 97% water, preferably from 50% to 95%, most preferably 65% to 90%.

10. A composition according to claims 2-9 having a pH of from 9 to 12, preferably 10 to 11.

11. A method of manufacturing a composition according to any of the preceding claims, wherein the ingredients constituting the composition are mixed with water, whereby the magnesium water from said water are complexed in situ.

12. A method of using a composition according to claims 1-10, wherein said composition is diluted in water, whereby magnesium ions from said water are complexed in situ, before it is applied onto a hard surface.

13. A method of using a composition according to claims 1-10, wherein a composition according to the present invention is applied onto a hard surface without having been diluted, and subsequently rinsed off of said surface with water, whereby magnesium ions from said water are complexed in situ.

14. A method according to claim 12 wherein said surface is not rinsed after said composition has been applied.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/11604

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C11D 1/12, 3/04
US CL :252/551, 550, 174.25, 170
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/550, 551, 174.25, 170

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: Magnesium (5A) ion #; Sulfate #; Detergent #

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>----<br>Y | US,A, 5,230,823 (Wise et al) 27 July 1993; see Abstractl; col. 6, lines 40-68; col. 7, line 1-col. 8, line 9, col. 11, lines 16-30; Example 3-4 and claims. | 1-3 |
| X<br>----<br>Y | US,A, 5,269,974 (Ofosu-Asante) 14 December 1993; see Abstract; col 3, lines 45-68; col. 4, line 51-col. 5, line 28; examples I-II. | 1-3 |
| Y | US,A, 5,320,783 (Marin et al) 14 June 1994, see col. 3, lines 4-66; col. 4, lines 30-68, col. 7, lines 28-42; examples I-IIII. | 1-3 |
| Y | US,A, 5,013,485 (Tsukuda et al) 07 May 1991; see col. 2, lines 18-54; col. 3, lines 6-20; examples I-II. | 1-3 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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