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(54) Hard surface cleaners.

(57) The present invention relates to foaming hard surface cleaners, and containers comprising the same in an enclosure. It is known, to provide foaming hard surface cleaners in a metal can together with a propellant to dispense the cleaner. Corrosion may occur on the interior surface of the can, in regions where the can contacts the liquid phase and more especially in regions where the can contacts the vapour phase (ie. in the headspace) and it is known to include in the composition a volatile amine, preferably a primary or secondary amine or ammonia. It is desirable to prevent corrosion in the gas phase while maintaining an acceptable product fragrance. In the compositions disclosed herein, adequate head space corrosion protection is attained with lower armonia levels, by inverting the can after filling and holding the can in an inverted position for a sufficient length of time for a protective film to form in the eventual upper region of the can and subsequently reverting the can to a conventional attitude to complete formation of a protective film in the lower region of the can.

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The present invention relates to foaming hard surface cleaners and a process for preparing the same in packaged form.

It is known, to provide foaming hard surface cleaners in a metal can together with a propellant to dispense the cleaner through a valve. Such cleaners normally comprise a surfactant (to provide a detergent action), a solvent (to assist in cleaning), a sequestrant for metal ions such as EDTA (to aid in the removal of limescale/iron stains) and a perfume. The pH of such compositions is alkaline. Known, commercially available compositions, are sprayed onto a hard surface, such as bathroom and kitchen surfaces, to facilitate the removal of limescale, soap deposits and other soiling. The cans are conventionally formed from tinned steel plate although other metals such as aluminium may be used.

It is known that corrosion may occur on the interior surface of the can, both in regions where the can contacts the liquid phase and more especially in regions where the can contacts the vapour phase (ie. in the headspace of the can). Corrosion in the headspace is believed to be caused by the presence of water vapour in the propellant of the headspace. Corrosion not only leads to a weakening of the can, but can also lead to a significant discolouration of the can contents requiring partially used cans to be discarded. Such discarding of cans needlessly releases surfactants and other materials into the ecosystem and generally wastes resources.

In known compositions, a high pH and alkaline silicates are used to prevent corrosion in regions of the can which contact the liquid phase. It is believed that corrosion is inhibited by the formation of a protective film on the inner surface of the can. With conventional tinned steel cans this layer is believed to comprise a layer of tin oxide on the inner surface of the can, although the precise composition of the layer is not known.

For the purposes of the present specification components present in the liquid phase which inhibit corrosion of the portion of the can in contact with the liquid phase will be referred to as liquid phase corrosion inhibitors.

Even in the presence of liquid phase corrosion inhibitors (such as alkaline silicate), corrosion can still occur in the regions of the can which contact the gas phase, particularly around the periphery of the upper domed portion of the can, in the upper portion of any side-wall seal and in the valve fitting. This second form of corrosion again leads to a weakening of the can and a significant discoloration of the can contents.

A further problem associated with corrosion is the loss of active sequestrant due to the release of metal ions into the composition. As sequestrant plays an important role in the lime-scale removing action of the composition this loss of sequestrant leads to a corresponding reduction in performance.

In order to prevent corrosion in those parts of the can contacted by the gas-phase, it is known to include in such compositions a volatile amine, preferably a primary or secondary amine or ammonia. For the purposes of the present specification ammonia is considered to be an amine unless the context demands otherwise.

It is well known that ammonia has a characteristic, persistent and undesirable odour, which requires a high level of strong perfume to be present in the composition In prior compositions, measured ammonia levels of up to and above 1000 ppm have been employed. The odour of ammonia is noticeable at levels above around 700-750 ppm. Odour assessment of hard surface cleaners in the marketplace reveals a noticeable and characteristically unpleasant odour of ammonia. Given the known threshold for the detection of ammonia by the human nose, it is believed that the ammonia levels in these prior products is always above 750 ppm.

Figures for the measured ammonia level in products obtained in the marketplace are expected to give lower analysed than actual values, possibly due to loss of vapour on opening the can for inspection and adsorption of ammonia onto the inner surface of the can.

From the above, it can be seen that it is known to prevent corrosion from occurring in the headspace of the can by the addition of ammonia to the formulation of the can contents. However, it is desirable to prevent said corrosion in the gas phase while maintaining an acceptable product fragrance and the known methods of preventing corrosion require the presence of unacceptably high levels of ammonia.

We have determined that adequate corrosion protection in the headspace of the can can be attained with lower levels of ammonia than were hitherto employed and that ammonia levels can be attained at which the odour of ammonia is either acceptable per se or can be effectively masked by a perfume.

In the compositions disclosed herein, adequate head space corrosion protection is attained with ammonia levels of above about 100 ppm, preferably above 190 ppm. In typical compositions, the odour of ammonia is not objectionable when ammonia is present at a level of below about 700-750 ppm, depending on the particular perfume composition being used.

It is also desirable to avoid EDTA as a sequestrant. EDTA is non-biodegradable and has been criticised due to its potential to sequester and solubilise heavy metal ions such as cadmium and mercury from river sludges and sediments. Surprisingly, we have determined that modification of the sequestrant system brings a benefit in reducing the extent of corrosion in the can while reducing any negative effects of sequestrant in the biosphere.

Accordingly, the present invention provides a stable, packaged, foaming hard surface cleaning composition wherein said composition comprises, a surfactant, a liquid phase corrosion inhibitor, 100-750 ppm volatile amine and is packaged in a metal can.

In the context of the present invention, acceptable storage stability is achieved if no significant corrosion of any part of the internal surface of the can occurs after 6 weeks storage at ambient temperature.

Generally, the composition further comprises a perfume.

With typical perfume compositions, a very acceptable odour is obtained when the amine is ammonia. Alternatively, the amine can be selected from the group comprising volatile mono, di and tri alkanolamines, amino-alcohols and mixtures thereof. Ammonia is preferred amongst the amines as it has a reduced tendency to form undesired compounds such as nitrosamines.

Preferably the ammonia level is 400-750 ppm, more preferably 400-600 ppm. Excellent results are obtained with ammonia levels of around 450-570 ppm. Lower levels of ammonia are generally preferred as any residual odour may be masked by low levels of a mild perfume.

Suitable liquid phase corrosion inhibitors comprises alkaline silicates. Alternatives can be employed provided that they are effective at the pH of the liquid phase and with the metal employed for the can wall. Suitable levels of liquid phase corrosion inhibitor range from 0.1-10%wt.

At progressively lower levels of ammonia, protection against corrosion in regions of the can which contact the vapour phase is progressively reduced. In the liquid phase, ammonia in combination with aqueous alkali, alkaline silicate or other liquid phase corrosion inhibitors, is effective in preventing corrosion at lower levels than in the vapour phase. Consequently compositions according to the present invention preferably comprise at least two corrosion inhibitors, one of which is more volatile and effective in the vapour phase the other of which is less volatile and effective in the liquid phase.

Preferably, the composition further comprises a sequestrant for metals. EDTA, is known as a suitable sequestrant, but it is preferred that the sequestrant is other than EDTA for the reasons given above.

Suitable sequestrants are selected from polycarboxylic acids, polyacrylates, phosphonates and salts thereof. Preferably, the sequestrant is a polycarboxylic acid or salt thereof. More preferably, the sequestrant is citric acid, or citric acid in combination with one or more acids selected from, adipic, succinic, glutaric acids or salts thereof. Most preferably, the sequestrant is citric acid alone or salts thereof.

In the presence of EDTA, the formation of a protective film on tinned steel cans is characterised by so-called de-tinning of the inner surface of the can. In the presence of citric acid salts, de-tinning of the inner surface of the can is not conspicuous, although corrosion is reduced significantly.

In prior cans the protective film does not extend to the upper or dome region of the cans. By ensuring that the protective effect extends over the inner surface of the can it is believed that corrosion of the can and hence discolouration of the product can be substantially reduced if not totally eliminated for the normal commercial lifetime of the can.

We have determined that the entire inner surface of a can may be protected by inverting the can after filling and holding the can in an inverted position for a sufficient length of time for a protective film to form in the eventual upper region of the can, and, subsequently reverting the can to a conventional attitude to complete formation of a protective film in the lower region of the can.

Other manipulative schemes such as rolling or shaking of the can, may be employed. The operative consideration being that the entire inner surface of the can is coated with the contents shortly after filling. It is believed that this treatment ensures that a protective layer is formed over the entire inner surface of the can.

Accordingly, a further aspect of the present invention subsists in a process for packaging a foaming hard surface cleaner which comprises the steps of:

a) filling the can with a composition comprising a liquid component comprising a liquid phase corrosion inhibitor and a normally gaseous component comprising a propellant and a volatile amine,

b) sealing the can,

c) storing the can in at least two orientations such that the entire inner surface of the can is treated with the liquid component.

In cans which have been treated by this "inversion process" or subjected to other re-orientation during storage, a characteristic double banding of the inner metal surface of the can, is observed when the can is laid open for inspection. In the case where the can is simply inverted, this double banding takes the form of a first and a second tide mark present on the inner surface of the can, each tide mark being in a first and second plane respectively which divides the inner volume of the can into a first and a second part, the arrangement being such that the volume of one of the parts bounded by the first plane is equivalent to the volume of one of the parts bounded by the other plane.

With tinned steel cans which have been subjected to the re-orientation process a characteristic dull film is also seen to extend over the entire inner surface of the can. In prior cans the protective film does not extend to the upper or dome region of the cans and these retain the shine of tinned steel plate. By ensuring that the protective layers cover the inner surface of the can it is believed that corrosion of the can and hence discolouration of the product can be substantially reduced if not totally eliminated for the normal commercial lifetime of the can.

The visibility of the film and the banding varies with the type of can employed and the sequestrant used. When EDTA is present as the sequestrant the banding is conspicuous and the interior surface of the can becomes quite dull. When citrate is used as the sequestrant, the banding may be barely visible and the interior surface retains a shine. Sufficient protection of the surface to prevent corrosion for the product lifetime is achieved with either citrate or EDTA as surfactant.

Taking the above-mentioned aspects of the present invention into consideration, it can be seen that package-stable, low-ammonia products may be manufactured which have an acceptable odour, and which do not suffer from the package corrosion problems which would otherwise occur at such low ammonia levels.

The various aspects of the present invention are unified in that while low ammonia formulations may have hitherto been desirable, it had not been possible in practice to package said formulations in stable form.

In preferred embodiments of the invention, the cleaning composition comprises at least ammonia, surfactant, solvent, sequestrant for metals, alkali, and a perfume.

Surfactant is conveniently present at a level of 0.1-10%wt, preferably 1-5%wt. Suitable surfactants are nonionics with a HLB in the range 3-20, preferably 12-16. Alcohol ethoxylates have been found particularly suitable as surfactants.

Solvents, are preferably capable of dissolving non-polar species and can be miscible or immiscible with aqueous solutions. Such solvents are preferably present at a level of 0.1-10%wt, preferably 1-5%wt. Solvents preferably have a solubility in water greater than 1%. Glycol ethers, preferably butyl carbitol and alcohols preferably isopropyl alcohol have been found suitable.

Sequestrant for metals such as calcium and magnesium is preferably present at levels of 0.1-8%wt, more preferably 0.5-6%wt. As mentioned above trisodium citrate is a preferable sequestrant.

Suitable alkalis include buffering agents which buffer at an alkaline pH. Sufficient buffer is preferably present to raise the pH of the composition to a pH in excess of 10. Preferably the pH of the composition falls into the range 11-13. Alkaline silicates, functioning as liquid phase corrosion inhibitors and buffering to a pH 11-12 are preferred. Alternative buffering systems comprise phosphates, carbonates and borates. The use of non-buffering agents to raise the pH, ie. the presence of sodium hydroxide is not hereby excluded. Alkaline silicate are also believed to have a stabilising effect on the formulations of the present invention.

Typical compositions are such that they comprise:

a) 100-750 ppm ammonia,
b) 0.75-10% citric acid or salt thereof,
c) 0.05-10% alkaline silicate, and,
d) 0.10-10% surfactant.

Alternative compositions comprise:

a) 100-750 ppm ammonia,
b) 0.1-5% amino polycarboxylic acid,
c) 0.05-10% alkaline silicate, and,
d) 0.10-10% surfactant.

Propellants are preferably present at levels of 3-20%. While halogenated propellants can be employed it is preferred to use an 'ozone-friendly' propellant such as compressed air, carbon dioxide, nitrogen and oxides thereof, a volatile hydrocarbon or mixtures of the same.

Mixtures of butane and propane have been found particularly suitable.

In order that the present invention may be further understood it will be described by way of example.

A foaming hard surface cleaner was prepared with the composition given in Table 1:

TABLE 1

Surfactant (Dobanol (RTM) 23/6.5)	2.50%wt
Solvent (Butyl carbitol)	2.00%wt
Sequestrant (Varies)	1.30-4.00%wt
Alkaline silicate	0.20%wt
Sodium Hydroxide	to pH 11.8
Perfume	0.40%wt
Ammonia	0-1000 ppm
Propellant (Propane/Butane)	6.00%wt
Water	to 100%

The alkaline silicate used was Crystal-120 A [Trademark] available in the marketplace from Crosfields of Warrington.

The process for packaging the foaming hard surface cleaner comprised the steps of:

a) filling a tinned steel can with a composition comprising ammonia, sequestrant, solvent, buffer, liquid phase corrosion inhibitor, perfume, and surfactant, mixed under air and dosed in 200 ml aliquots,

b) dosing the chilled propellant into the can and sealing the can, and,

c) storing the can in an inverted orientation for 48 hours after filling and then a 'normal' orientation such that the entire inner surface of the can is treated with the liquid phase corrosion inhibitor.

Cans were opened and the internal surface inspected after storage for a total of 6 weeks at ambient temperature.

At levels of 1000 ppm ammonia, excellent corrosion protection was obtained, in the presence of EDTA, (1.3%) with or without the inversion process, but the odour of ammonia evolved by the product was described as unacceptably unpleasant by testers. The odour and corrosion results for both control and inverted cans are summarised in Table 2 given below.

TABLE 2

NH3 (ppm)	**Corrosion**		**Odour**
	Control	**Inverted**	
0 (control)	yes	yes	acceptable
190	yes	no	acceptable
380	yes	no	acceptable
580	yes	no	acceptable
700	yes	no	acceptable
1000 (control	no	no	acceptable

It can be seen that excellent corrosion protection was obtained with 190-700 ppm ammonia. These examples constitute examples of the present invention whereas the examples with 0 and 1000 ppm ammonia are comparative examples.

Cleaning performance was compared on pre-soiled plastic sheets. The sheets were prepared by spraying a thin layer of solvent dispersed calcium stearate onto a sheet formed from acrylic plastic of the type used to manufacture bath-tubs. Prior to the application of the calcium stearate the sheet was cleaned with a proprietary dish-washing liquid and rinsed well with water. A solution of 15 gm of calcium stearate in 500 gm of isopropyl alcohol was employed so as to deposit approximately one gram of calcium stearate on a sheet having dimensions of 30 cm x 20 cm. A small quantity of carbon black was added to aid visualisation during the cleaning performance test. Subsequent to the application of the soil, sheets were baked at 50°C for 18 hours.

The performance test comprised the application of a hard surface cleaning composition to a pre-soiled sheet. Four, hollow, open ended, clear, glass cylinders, each 5 cm high/5 cm diameter were placed on the soiled surface of the sheet. The composition was sprayed into the open upper end of each cylinder for 2 seconds, half-filling the cylinders with foam. A time of five minutes was allowed for the passive cleaning operation. The cylinders were then lifted off the sheet and the sheet was gently rinsed in 12 French running cold water (15°C) for 10 seconds. The flow rate of the water was set at 2 litres/minute prior to rinsing. The sheets were left to dry in air at room temperature (this takes 1-2 hours) then three replicates of each composition were assessed by a trained panel of at least three persons using the scale indicated in Table 3.

TABLE 3

CLEANING PERFORMANCE		
Rank	**Score**	**Effect**
Best	4	75-100% clean
	3	50-75% clean
	2	25-50% clean
Worst	1	0-25% clean

Results of the panellists and replicates were averaged to obtain an overall percentage for each composition.

Comparative trials were performed with the sequestrants given in Table 4. Results were normalised for a 1.3% EDTA effectiveness of 100%. The normalised figure is the overall composition scores in the performance test specified above, using the ranking in Table 3 averaged over the replicates.

For comparative purposes, the affinity for calcium of some sequestrants is given as the log of the binding constant between calcium and the sequestrant at constant concentration of sequestrant and calcium. These figures should be considered to be indicative of the relative calcium binding performance rather than as absolute values.

TABLE 4

% EDTA effect		Aff. ca
EDTA 1.3%	100	9.7
EDTA 0.0%	48	-
Citrate 5.0%	109	3.5
Citrate 4.0%	106	-
Citrate 3.0%	76	-
Dequest 2016 1.0%	139	4.6
Dequest 2060s 1.0%	122	7.1
Dequest 2000 1.0%	68	6.3
Sokalan DCS 3.0%	52	-
Trilon ES9910 1.5%	106	5.6
PA 25 PN 1.5%	35	-
PA 40 1.5%	35	-
Solakan CP5 1.5%	35	-
Sokalan CP10 1.5%	70	-

Dequest, Sokalan and Trilon are trademarks.

It can be seen from Table 4 that the effectiveness of a sequestrant is not simply related to the calcium binding ability: ie. the Dequest 2016/2060s/2000 sequestrants have affinities for calcium which do not differ in the same way as their effectiveness in the cleaning test ie. Dequest 2060s appears to have the highest affinity for calcium on a theoretical basis whereas the Dequest 2016 apparently has a lower affinity but forms a more effective cleaning composition according to the experimental results.

It was noted that, in the presence of both ammonia and EDTA, the formation of a protective film on tinned steel cans is characterised by so-called de-tinning of the inner surface of the can. In the presence of citric acid salts in combination with ammonia and the silicate, de-tinning of the inner surface of the can is not conspicuous, while corrosion is reduced considerably. Surprisingly, citric acid performed far better that Sokalan DCS which is a combination of adipic, succinic and glutaric acid.

In the presence of ammonia and citric acid salts without silicate being present, de-tinning was again noted.

Various modifications may be made to the embodiments of the present invention without departing from the scope of the invention when considered in a broad form. For instance, while the invention has been described with reference to a can requiring a propellant to dispense the contents, the use of a pump-action dispensing closure is not hereby excluded.

Claims

1. Stable, packaged, foaming hard surface cleaning composition wherein said composition comprises, a surfactant, a liquid phase corrosion inhibitor, 100-750 ppm volatile amine and is packaged in a metal can.

2. Composition according to claim 1 wherein the liquid phase corrosion inhibitor is an alkaline silicate.

3. Composition according to claim 1 or 2 further comprising a perfume.

4. Composition according to any one of claims 1 to 3 wherein the volatile amine is ammonia.

5. Composition according to any of claims 1 to 4 having a pH in the range 11-13.

6. Composition according to any of claims 1 to 5 comprising 190-750, preferably 400-750 ppm, more preferably 450-570 ppm ammonia.

7. Composition according to any of claims 1 to 6 wherein the metal can contains a propellant gas.

8. Composition according to claim 1 wherein a first and a second tide mark are present on the inner surface of the can, each tide mark being in a first and second plane respectively which divides the inner volume of the can into a first and a second part, the arrangement being such that the volume of one of the parts bounded by the first plane is equivalent to the volume of one of the parts bounded by the other plane.

9. Process for packaging a foaming hard surface cleaner which comprises the steps of:
a) filling the can with a composition comprising a liquid component comprising a liquid phase corrosion inhibitor and a normally gaseous component comprising a propellant and a volatile amine,
b) sealing the can,
c) storing the can in at least two orientations such that the entire inner surface of the can is treated with the liquid phase corrosion inhibitor.

10. Composition according to any one of claims 1 to 6 comprising 100-750 ppm ammonia, an effective level of a liquid phase corrosion inhibitor, 0.1-10%wt surfactant, 0.1-8%wt sequestrant for metals and a perfume.

11. Composition according to any one of claims 1 to 6 wherein the sequestrant is selected from polycarboxylic acids, polyacrylates, phosphonates, salts thereof and mixtures thereof.

12. Composition according to claim 11 wherein the sequestrant is a polycarboxylic acids or salt thereof.

13. Composition according to claim 12 wherein the sequestrant is citric acid or a salt thereof.

14. Composition according to claim 13 comprising:
a) 100-750 ppm ammonia,
b) 0.75-10% citric acid or salt thereof,
c) 0.05-10% alkaline silicate, and,
d) 0.10-10% surfactant.

15. Composition according to claim 10 comprising:
a) 100-750 ppm ammonia,
b) 0.1-5% amino polycarboxylic acid,
c) 0.05-10% alkaline silicate, and,
d) 0.10-10% surfactant.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 31 1276

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 124 143 (UNILEVER) * the whole document *	1	C11D17/00 C11D3/00 C11D3/08 C11D3/20 C11D3/33
A	FR-A-2 469 450 (SOLITAIRE PRODUITS D'ENTRETIEN FRANÇAIS-PRODEF.) * page 1, line 1 - page 7, line 30 *	1-15	
A	US-A-3 915 633 (RAMACHANDRAN) * the whole document *	1-14	
A	US-A-3 296 147 (GATZA) * claims 1,2 *	1	
A	CHEMICAL ABSTRACTS, vol. 103, no. 6, 12 August 1985, Columbus, Ohio, US; abstract no. 38978, XU, XUEWEN ET AL. 'Surface-active chelants - amido acids as inhibitors in water' * abstract * & HUADONG HUAGONG XUEYUAN XUEBAO, (4), 485-93 1984, -----	15	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06 APRIL 1993	DELZANT J-F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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