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(54) IMPROVEMENTS IN GENERAL PURPOSE CLEANING COMPOSITIONS

VERBESSERUNGEN IN ALLZWECKREINIGERZUSAMMENSETZUNGEN

AMELIORATIONS RELATIVES A DES COMPOSITIONS NETTOYANTES POLYVALENTES

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DescriptionTechnical Field

5 **[0001]** The present invention relates to improvements in general purpose cleaning compositions for household use.

Background to the Invention

10 **[0002]** General purpose household cleaning compositions for household use are commercially available in both powdered and liquid form.

[0003] Powdered cleaning compositions consist mainly of builder or buffering salts such as phosphates, carbonates, silicates etc. Such compositions display good inorganic soil removal, but they can be deficient in cleaning ability on organic soils such as the calcium and/or magnesium salts of fatty acids and fatty/greasy soils typically found in the domestic environment. Such compositions generally form solutions buffered at an alkaline pH by the builder. It is generally believed that alkaline pH facilitates the detergency of free fatty acids by conversion of the fatty acids into the corresponding soap.

15 **[0004]** Liquid cleaning compositions generally comprise an organic solvent and have the great advantage that they can be applied to hard surfaces in neat or concentrated form so that a relatively high level of surfactant material and organic solvent is directly delivered onto the soil. These liquid compositions are of particular utility in the cleaning of hard surfaces such as floors and walls and kitchen or bathroom surfaces as well as being useful in cleaning soft furnishings such as upholstery, carpets, curtains etc. Again, these compositions are generally buffered alkaline although neutral compositions are known and some acidic compositions have been marketed as specialist bathroom cleaners.

[0005] Both of the above-mentioned types of compositions may comprise organic acids, such as citric, adipic or glutaric acids.

20 **[0006]** Typically, the surfactants used in commercial general purpose cleaners include one or both of linear alkyl benzene sulphonates (ABS) and secondary alkane sulphonates (SAS).

[0007] The incorporation of certain surfactants into such solvent/water compositions presents no difficulties when these surfactants are present at relatively low concentrations. European Patent EP 0344847 (P&G), for example, discloses compositions comprising butoxy-propanol solvents in combination with up to 5%wt sodium linear C8-C18 alkyl benzene sulphonate.

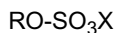
[0008] Mixtures of linear alkyl benzene sulphonates with alcohol ethoxylates and optionally small amounts of fatty soaps comprise the surfactant system used in a number of successful, liquid, alkaline, commercial products having an in-product pH of 8-11.

25 **[0009]** In addition to the removal of fatty/greasy soil, it is desirable that household cleaning compositions should have the ability to remove limescale. Limescale largely consists of calcium and magnesium carbonates, which are present as the corresponding bi-carbonates at varying levels in natural waters and form the carbonate on crystallisation by disproportionation. It is well known that carbonates are soluble in acidic solutions. However, for the reasons given above, it is believed that acid compositions are less effective than alkaline compositions.

[0010] A further outstanding technical problem with such compositions is that the surfactants most commonly used, are less biodegradable and consequently less preferable environmentally than other surfactant systems.

30 **[0011]** In particular, primary alcohol sulphate (hereinafter referred to as PAS) is an environmentally desirable anionic surfactant, both due to its ease of biodegradability as compared with linear alkyl benzene sulphonates and secondary alkane sulphonates and the fact that it can be derived from natural materials such as coconut and other vegetable oils as a source of fatty acid residues.

45 **[0012]** Primary alcohol sulphate comprises a mixture of materials of the general formulation:



50 wherein R is a C₈ to C₁₈ primary alkyl group and X is a solubilising cation. Suitable cations include sodium, magnesium, potassium, ammonium, TEA and mixtures thereof.

[0013] The use of the salts of PAS in combination with other surfactants is well known from the literature.

[0014] EP 125711 (Clarke: 1984) relates to GPC's containing nonionic, anionic (examples are Mg-PAS) and a partially esterified resin.

55 **[0015]** GB-2160887 (Bristol Myers: 1984) relates to GPC's which comprise solvent, anionics including alkali metal, magnesium, ammonium and TEA-PAS salts and 0.005-3.0% of a nonionic including 75-100% on nonionic of a water insoluble nonionic. The sodium salt of the lauryl sulphate (Na-C₁₂ PAS) is the most preferred anionic surfactant.

[0016] GB 2144763 (P&G: 1983) relates to cleaning composition in the form of a microemulsion, comprising at least 5% solvent and a magnesium salt. The preferred compositions comprise mixtures of nonionic surfactants, paraffin

sulphonates, alkyl sulphates (PAS), ethoxylated phenols and ethoxylated alcohols.

[0017] EP 107946 (P&G: 1982) relates to liquid detergent (dishwashing) compositions comprising 6-18% Mg-PAS, together with a water soluble C₁₃-C₁₈ alkane or alkene sulphonate and a water soluble alkyl ether sulphate.

[0018] The above-mentioned surfactants, ABS, SAS and PAS are very effective foaming surfactants. While the formation of foam is desirable with many personal washing products, such as shampoos and bar soaps, the presence of foam is often undesirable in fabric washing and surface cleaning operations, as foam can be difficult to remove after the cleaning operation. For this reason antifoams have been included in formulations. Calcium soaps, i.e. the calcium salts of fatty acids are well known as an antifoaming component in -fabric washing compositions and in hard surface cleaning compositions.

[0019] The use of the combination of hydrocarbons and calcium sensitive, fatty acid soaps as antifoam systems for powder compositions has been disclosed in GB 1099562 (Unilever: 1964). In that citation are disclosed powdered detergent compositions which comprise anionic sulphate or sulphonate detergents, alkaline polyphosphates and a 'suds-depressant' mixture of a hydrocarbon and a fatty acid having from 12 to 31 carbon atoms. The hydrocarbon is broadly defined, as including straight or branched chain alkanes (liquid paraffin oils in 1:1 admixture with high melting paraffin waxes having a boiling point above 90 Celcius), alkenes, alkylated benzene, condensed aromatics such as naphthalene and anthracene and their alkylated derivatives and alicyclic hydrocarbons, including terpenes and like compounds. Preferred hydrocarbons include those materials having a boiling point above 90 Celsius, such as the aforementioned mixtures of paraffin oils and waxes, dodecyl benzene and turpentine oil.

[0020] The use of the combination of solvents, soaps and selected terpene solvents as antifoam systems for liquid hard surface cleaning compositions is further disclosed in EP 0080749 (P&G: 1982). In these compositions unlike, for example, carpet cleaning compositions, it is advantageous that the product can be used at will without the step of adding a separate antifoam component.

[0021] More specifically, EP 0080749 teaches the use of mono (two isoprene units) or sesqui- (three isoprene unit) terpenes in combination with both a specified solvent (2-(2-butoxy-ethoxy) ethanol: available in the marketplace as BUTYL CARBITOL [RTM]) and 0.05-2%wt of one or more of the alkali, ammonium and alkanol-ammonium soaps of C₁₃-C₂₄ fatty acids as an antifoam system. In this citation, these three components are said to interact so as to have an antifoaming activity.

[0022] The preferred terpenes as disclosed in this citation are the mono and bi-cyclic terpenes of the 'hydrocarbon class' of terpenes such as terpinenes, terpinolenes, limonenes, pinenes and the so-called 'orange' terpenes as obtained from the skins of oranges. Other terpenes including the terpene alcohols, aldehydes and ketones are less preferred.

[0023] Terpenes and related compounds suffer from the general disadvantages that they are relatively expensive raw materials and odiferous compounds and generally lend a pine-like or lemon-like odour to products. It is desirable that the base formulation of cleaning compositions should have a low odour or be odour free. Moreover, terpenes may contain traces of so-called 'musk xylenes' and doubts have been raised as to the physiological acceptability of these materials.

[0024] Products intended for use as bathroom cleaners should form a relatively stable, clinging foam in the initial stages of cleaning. This foam provides a visible indication of the parts of the surface to which the cleaner has been applied. More importantly, the foam clings to the surface and prevents run-off, thereby minimising the quantity of surfactant containing product which is required and consequently minimising both cost and the release of surfactants into the environment. However, it is desirable, so as to facilitate use and assist in the conservation of water, that the composition should be rinsable using, in so far as possible, a minimal quantity of water and little effort.

[0025] Considering all of the above, it can be seen that an ideal household cleaning composition should form a relatively stable foam on application to a surface and rapidly defoam when rinsed from the surface. Such compositions should not contain environmentally or physiologically unacceptable components and should not require the addition of special antifoaming components to the rinsing water. While specialist cleaning compositions meeting many of these needs separately have been marketed or suggested in the literature a need exists for a general purpose cleaner which has the advantages of an acid cleaner against limescale but which is also effective against a wide range of soils.

Brief Description of the Invention

[0026] We have found that selected fatty acids have a foam-boosting effect in certain concentrated formulations and a foam depressing effect when said formulations are diluted with mildly alkaline water. Where these fatty acids are combined with polycarboxylic acids, solvents and surfactants, at acid pH, remarkably simple combinations of components produce compositions which show excellent cleaning on a wide range of soils and show excellent rinsing behaviour.

[0027] Accordingly, the present invention subsists in an aqueous cleaning composition comprising:

- a) 1-40%wt of a surfactant system comprising at least one anionic surfactant other than an alkali metal salt of a fatty

acid,

b) 0.1-3%wt a C10-C22 monocarboxylic fatty acid,

c) 1-30%wt of a semi-polar solvent which has dielectric constant of from 5-35,

d) 1-10%wt of polycarboxylic acids or salt thereof, and,

e) a base, in an amount sufficient that said composition has a pH of less than the pK_a of the monocarboxylic fatty acid and less than 6.

Detailed Description of the Invention

[0028] As mentioned above, we have determined that, surprisingly, the C10-22 fatty acids have a foam boosting effect in the compositions of the present invention. This is expressed as an improved 'cling' of the foam to sloping or vertical surfaces. Thus the compositions according to the present invention are particularly well suited for use as hard surface cleaning compositions.

[0029] Without wishing to limit the invention by reference to a theory of operation, it is believed that, at a pH which is below the pK_a of the monocarboxylic fatty acid, the foam boosting effect is observed. The precise pK_a of the fatty acid is difficult to confirm in practice as the fatty acids are not water-soluble under these conditions, although a close estimate of the pK_a can be obtained by titration. It is also believed that the pH of the composition should be above the lowest pK_a of the polycarboxylic acid, such that the polycarboxylic acid exists in a partially ionised form.

[0030] Domestic water supplies generally contain some dissolved calcium, derived from minerals at typical levels ranging from 20-400 ppm. (2-40 degrees French). Waters having higher levels of calcium are known but are relatively rare.

[0031] Domestic water supplies typically have a slightly alkaline pH of above 7.5, typically around 8 and principally due to dissolved bicarbonate as is naturally present in the water. In a few exceptional cases, alkali forming components, such as calcium oxide may be added to the water supply so as to neutralise acidic waters and thereby prevent dissolution of lead and other potentially toxic metals from pipes and fittings.

[0032] On addition of several volumes of calcium-containing alkaline domestic water to compositions of the present invention, it is believed that the alkalinity of the water raises the pH of the originally acid system to a point above the pK_a of the fatty acid and causes the fatty acid to ionise whereupon a precipitate of the fatty acid is formed with the calcium present in the water thereby forming a calcium soap. This precipitate has an antifoam effect in the known manner and is consequently believed to assist rinsing of the product.

Solvents

[0033] Semi-polar solvents are essential components of the present invention. As will be shown hereinafter by way of example, the presence of solvent is believed to potentiate the foam boosting effect of fatty acid in acidic solution and potentiate the anti-foam effect of fatty acid in alkaline solution.

[0034] Solvents have a dielectric constant of from 5-35.

[0035] Preferably, the solvent is selected from: propylene glycol mono n-butyl ether, dipropylene glycol mono n-butyl ether, propylene glycol mono t-butyl ether, dipropylene glycol mono t-butyl ether, diethylene glycol hexyl ether, ethyl acetate, ethanol, isopropyl alcohol, ethylene glycol monobutyl ether, di-ethylene glycol monobutyl ether and mixtures thereof.

[0036] Preferred solvents are the glycol ether solvents and these are preferably selected from the group comprising propylene glycol mono n-butyl ether (available as 'Dowanol PnB' [RTM]) and di-ethylene glycol monobutyl ether (available as 'Butyl Digol' [RTM] or 'Butyl Carbitol' [RTM]). These solvents are particularly preferred due to cost, availability and safety factors. We have determined that this selection of solvents gives enhanced cleaning performance as regards inks and dyestuffs and improved product stability as well as potentiating the antifoaming behaviour of the compositions on rinsing.

[0037] Preferred ranges for the total surfactant:solvent ratios fall in the range 1:1 to 10:1, preferably 2:1 to 5:1. The narrower ratio range is preferred for reasons of cost and product stability. Solvent contents are 1-30%wt of the composition, preferably 2-20% of the composition, in order to achieve an effective solvent concentration on dilution of the concentrates.

Buffers

[0038] Buffers are essential components of the compositions according to the present invention.

[0039] It is believed that, the presence of a buffer is essential to ensure that the pH of the undiluted composition is maintained at an acidic pH, below the pK_a of the fatty acid. However, the pH must not be so strongly buffered that excessive addition of water is required to raise the pH above the pK_a of the fatty acid.

[0040] Moreover, while strongly acid solutions should be avoided so as to reduce damage to surfaces being cleaned, some reserve of acidity is required such that the foam is not so rapidly destabilised by the formation of insoluble calcium soaps to reduce the limescale removing effect of the compositions.

[0041] The preferred buffer system comprises a polycarboxylic acid and a base selected from ammonium or alkali metal hydroxides and/or organic amines can also be used. Ammonium hydroxide is particularly preferred as it is believed to give enhanced calcium soap scum removal although sodium hydroxide also gives good results. Preferably, such a system will buffer the product at a pH 2-6.

[0042] It is preferable that the buffer system is such that the pK_a of the fatty is reached on addition of more than ten volumes of water on product. The alkalinity and hardness of the water added will have some effect on the quantity of water required to raise the pH above the pK_a .

[0043] For typical surfactant contents of 4-6%wt on product, the buffer system should be selected such that the pH is raised above the pK_a of the fatty acid when less than 1000 volumes of water are added.

[0044] A particularly preferred product pH range is pH 3.14-4.9, a pH around 4 is most preferred as certain enamels are sensitive to pH below 3 and products having a low pH can take excessive rinsing to neutralise the composition with waters of low alkalinity. The presence of polycarboxylic acids as salts in the formulation rather than as the acid form is believed to lead to a better foam so it is preferred that the pH of the composition should be above the lowest pK_a of the polycarboxylic acid present. Citric acid, the preferred polycarboxylic acid, has pK_a 's of 3.14, 4.77 and 6.39 and consequently pH's above 3.14 are preferred.

Sequesterants

[0045] Weak sequesterants in the form of organic polycarboxylic acids are essential components of the compositions according to the present invention. The presence of these weak sequesterants improves cleaning performance. It is believed that these components sequester weakly bound calcium ions which are involved in the attachment of soil to surfaces and thereby facilitate the removal of these soils.

[0046] Strong sequesterants can also be present. However sequesterants such as EDTA are less preferred for environmental reasons, as it has been suggested such poorly biodegradable sequesterants can solubilise heavy metals from river-bottom deposits. Moreover EDTA and other strong sequesterants have a tendency to complex with the calcium present in the domestic water and prevent the formation of the defoaming calcium soap mentioned above.

[0047] Preferably, the sequesterant is selected from, citric, adipic, succinic, malaeic, glutaric acids, mixtures thereof or salts thereof. Levels of sequesterant range from 1-10%wt, preferably 3-6%wt on product.

[0048] Most preferably, the sequesterant is citric acid or salts thereof. Citric acid is a weak sequesterant for calcium, available from renewable resources and is rapidly biodegradable.

[0049] Citric acid is particularly preferred as both the sequesterant and a component of the buffering system, at preferable inclusion levels of 3-6%wt on product.

Fatty Acids

[0050] C10-C22 fatty acids are essential components of the compositions according to the present invention.

[0051] It is believed that shorter chain fatty acids would not form sufficiently insoluble calcium soaps and longer chain fatty acids would be too insoluble in the composition to function as an antifoam component. Moreover, these mid chain length fatty acids are commercially available at reasonable cost and are derived from renewable resources.

[0052] The fatty acids may be linear or branched, saturated or unsaturated, but are preferably linear fatty acids obtained from nature.

[0053] C12-C16, preferably 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 soaps are less soluble in the absence of expensive hydrotropes or organic solvents.

[0054] Levels of fatty acids range from 0.1-3% on product, with a range of 0.5-1%wt being particularly preferred.

[0055] It is important that the pH of the composition is below the pK_a of the fatty acid being employed. In general, the pK_a of a C12-C16 fatty acid will be close to 4.9, consequently the pH of the compositions will be below this figure. Considering the requirement that the pH is above the pK_a of the polycarboxylic acid, the pH of the composition will generally be in the range 3.14-4.9.

Surfactants

[0056] At least one anionic surfactant other than soap is an essential component of compositions according to the present invention.

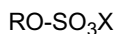
[0057] Preferably the surfactant comprises one or more of the group comprising: primary and secondary alcohol

sulphates, alcohol alkoxy sulphates, primary and secondary alkane sulphonates and alkyl aryl sulphonates. In the absence of the anionic surfactant the products according to the present invention exhibit less effective cling.

[0058] Preferably, the ratio of fatty acid to anionic surfactant falls into the range 1:4 to 1:20, with particularly preferred around 1:5-1:10, expressed as wt% fatty acid to wt% anionic surfactant on product. This achieves a good balance between foaming and cleaning performance.

[0059] Preferably the anionic surfactant is a primary alcohol sulphate (PAS), a foaming, readily biodegradable, surfactant.

[0060] The preferred primary alcohol sulphate (PAS) comprises a mixture of materials of the general formulation:



wherein R is a C₈ to C₁₈ primary alkyl group and X is a solubilising cation. Suitable cations include sodium, magnesium, potassium, ammonium and mixtures thereof.

[0061] We have determined that compositions which comprise magnesium PAS and organic acid, partially neutralised with a base have improved cleaning effectiveness especially as regards lime soaps and lime scales whilst maintaining cleaning efficiency against fatty/greasy soils. Consequently, particularly preferred embodiments of the present invention comprise magnesium, at a Molar ratio of 0.1-0.8 moles Mg per mole primary alcohol sulphate present.

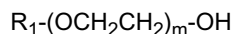
[0062] It should be noted that the sole use of magnesium as the counter-ion for the PAS can lead to difficulties in the presence of the polycarboxylic acid, it is therefore preferable that the Molar ratio of counterions for the PAS is such that around the ratio of Mg to other counterions does not exceed around 5:1. MgPAS to NaPAS ratios of more than 1:1 but less than 2:1 are preferred.

[0063] Particularly preferred PAS molecules are those with a major proportion of C₁₀-C₁₄ alkyl residues.

[0064] As mentioned above, these surfactants can be obtained by forming the primary alcohol sulphate from fatty acids obtained from renewable resources such as coconut oil although they can also be obtained from synthetic alcohol sources. These surfactants show very acceptable biodegradation behaviour.

[0065] Suitable additional surfactants are selected from cationic, nonionic, amphoteric and zwitterionic surfactants as well as mixtures thereof.

[0066] The presence of nonionic surfactants is particularly advantageous. The preferred nonionic surfactants are alkoxyated alcohols and the preferred alkoxyated alcohols are selected from the group comprising ethoxyated alcohols of the general formula:



wherein R₁ is straight or branched, C₈ to C₁₈ alkyl or hydroxyalkyl and the average degree of ethoxylation m is 1-14, preferably 3-10 for good fatty soil detergency.

[0067] The starting materials for the synthesis of these ethoxyated alcohols, a minor component of the surfactant system, are available from both natural and synthetic sources.

[0068] Most preferably the surfactant system comprises a mixture of primary alcohol sulphates and alkoxyated alcohols. For the purposes of this specification alkoxyated alcohols are taken to include alkyl or hydroxy-alkyl ethoxyated alcohols.

[0069] Preferably the primary alcohol sulphates and alkoxyated alcohols are present in a ratio of from 3:1 to 1:1, with a ratio of around 2:1 being particularly preferred.

[0070] Particularly preferred compositions comprise 15-30% primary alcohol sulphate and 5-15% nonionic surfactant. These relatively high levels of PAS and nonionic surfactant are desirable in order to form concentrated compositions which can be transported more efficiently and require less packaging material.

[0071] Overall levels of surfactant comprise 1-40%wt of the product, with levels of 2-10% being preferred for household use as non-concentrates. Surfactant levels of 20-40%, more preferably 25-35%, are preferred for concentrates although at the very highest surfactant levels additional antifoam components may be required.

Minors and Other Inessentials

[0072] The compositions of the invention can further comprise other minor components selected from the group comprising: perfumes, colours and dyes, hygiene agents, viscosity modifiers and mixtures thereof. In certain embodiments of the invention it is useful to include further foam control agents in the formulation.

[0073] Preferably the further foam control agents comprise hydrophobic oils. More preferably, the hydrophobic oil is a linear or branched chain hydrocarbon or silicone oil, even more preferably the hydrophobic oil is a paraffin.

[0074] Most preferably, the hydrophobic oil is a paraffin with a 50%wt loss boiling point in the range 170-300, Celsius. The term 50% loss boiling point being intended to indicate that 50% of the weight of the paraffin can be distilled

off at a temperature within this range. In general the limits of boiling points of paraffin suitable for use in the composition of the present invention lie between 171 and 250 Celsius. We have found that the isoparaffins, i.e. branched chain paraffins, are particularly effective when compared with other hydrophobic oils such as n-decane and n-tetradecane.

[0075] The solubilised hydrophobic oil content of embodiments of the present invention is typically in the range 0.2-5wt%, preferably 1.0-2.0wt%. Where hydrophobic oil is present the preferred ratio of fatty acid to hydrophobic oil is in the range 0.5-1:1-0.5, preferably about 1:1. These proportions form a particularly effective antifoam system.

[0076] Preferably compositions according to the present invention are homogeneous, more preferably translucent and most preferably transparent. Typical viscosities are 1-2000 mPas at a shear rate of 21 s^{-1} as measured at 25°C.

10 Packaging

[0077] It is preferable that the compositions of the present invention are provided in a package adapted to produce a spray of the product, preferably a spray of foam, although the possibility of other dosing and delivery systems is not intended to be excluded.

15 **[0078]** Having regard to all of the above, preferred embodiments of the present invention comprise an acidic aqueous cleaning composition comprising:

a) 2-40%wt surfactant, said surfactant comprising primary alcohol sulphate and preferably one or more nonionic surfactant wherein at least 50%wt of the surfactant present is primary alcohol sulphate, as principal surfactant

20 b) 0.2-5%wt C10-18 unbranched fatty acid as a foam booster in acidic conditions and an antifoam in alkaline conditions.

c) at least one solvent selected from the group of glycol ether and 1-5 carbon alcohol solvents, in an amount such that the surfactant:solvent ratios fall in the range 1:1 to 10:1,

25 d) 1-10%wt of a water soluble organic acid, selected from citric, adipic, succinic, glutaric, maleic acids, salts thereof or mixtures thereof, as a calcium and magnesium sequesterant and buffering component, and,

e) sufficient base to bring the pH of the composition into the range 3.14-4.9,

[0079] In order that the present invention may be further understood it will be illustrated hereafter by means of examples and with reference to the accompanying drawings wherein:

30

Figure 1: shows the effect of formulation on the number of rinses required to reduce foam volume with waters of differing hardness.

Figure 2: shows the effect of pH on foam volume with waters of differing hardness.

35 Examples 1-2

[0080] Compositions were prepared according to Table 1 as below. All components were mixed at room temperature and filled into bottles equipped with trigger spray heads. The nonionic surfactant was DOBANOL 23-6.5 EO (RTM ex. SHELL), the PAS was DACPON-27L (RTM ex. DAC). Butyl Carbitol is a trademark of Union Carbide. The fatty acid was PRIFAC 7901 (RTM ex. Unichema).

40

TABLE 1

	EXAMPLE 1	EXAMPLE 2
citric acid	4.00%	4.00%
pas	4.00%	4.00% (anionic)
nonionic	2.00%	2.00%
butyl carbitol	2.00%	2.00% (solvent)
perfume	0.50%	0.50%
sodium hydroxide	1.20%	1.20%
preservative	0.015%	0.015%
fatty acid	-	0.5%

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TABLE 1 (continued)

	EXAMPLE 1	EXAMPLE 2
water	to 100%	to 100%
pH	4.3	4.3
cling	2.7	3.6

[0081] Performance was evaluated by spraying the products onto a non-horizontal surface and rinsing with hard water (typically >26 French). 'Cling', was estimated by a panel of 20 trained technicians instructed to rate the foam cling in a blind test on a scale of 1-5 with 1 representing poor cling and 5 representing excellent cling.

[0082] Example 1 is a commercially available product selected as a comparative example; the performance of this product was good.

[0083] Example 2 is an example of the present invention, this formulation showed a more voluminous and clinging foam, which was especially effective as regards adhesion to inclined or vertical surfaces. While the composition of example 1 showed acceptable cling and could be rinsed without particular difficulty, it was found that the composition of example 2 showed improved cling and rinsed with exceptional ease.

Examples 3-8

[0084] Figure 1 shows the effect of formulation on the number of rinses required to reduce foam volume with waters of differing hardness.

[0085] Measurements were performed as follows, 5gm of product was diluted to 50ml with water of the indicated hardness in a graduated separating funnel with the valve closed. The funnel was vigorously shaken by hand, for approximately ten seconds to produce a foam, and the initial foam volume noted after excess liquor had been run out via the valve. Aliquots of 50ml of water are used for each rinse, being added into the funnel, with a further shaking cycle and a further measurement of the foam volume after removal of the liquor. This procedure is repeated until no foam remains. Compositions employed were as examples 1 and 2 above, with a fatty acid level of 0.5%.

[0086] From the figure, it can be seen that the addition of fatty acid to the comparative example resulted in a reduction of the number of rinsing cycles required in all cases, and that the improvement was more marked for harder waters.

[0087] Figure 2 shows the effect of pH on foam volume with waters of differing hardness. The pH mentioned is the pH of the liquor obtained during the rinsing cycles described above. It can be seen that as rinsing progresses, the pH of the liquor rises. It can be seen that for water containing an exceptionally high level of calcium the effect of the fatty acid was very marked. For more commonplace waters the foam volume fell rapidly once the pH had risen above 6.5 from the original product at 10% dilution pH of 4-5.

[0088] From the above examples it can be seen that the exemplified composition shows both improved foam cling and improved rinsing as compared with the composition of the prior art.

Examples 9-15

[0089] Table 2 below, gives data for compositions according to example 2 in which the average chain length of the fatty acid was varied. Data for the composition of Example 1, without fatty acid is given for comparative purposes. Cumulative foam volume, ('CFV') is measured in cubic centimetres for a standard initial volume and shaking protocol as described above with reference to examples 3-8. The CFV indicates the total volume of foam generated in the rinsing process, using water of 26 French hardness. Number of rinses required to eliminate the foam was determined as described above.

TABLE 2

	FATTY ACID	CFV	RINSES
Ex.9	Ex.1	4950	9.5
Ex.10	C8	3025	8.5
Ex.11	C10	2400	8.0

TABLE 2 (continued)

	FATTY ACID	CFV	RINSES
Ex. 12	C12	2525	5.0
Ex. 13	C14	400	4.0
Ex. 14	C18	375	6.0
Ex. 15	C22	975	6.0

[0090] From the above data it can be seen that fatty acids having a chain length of >C12 markedly reduce the CFV. It was noted that fatty acids having a chain length >C22 were insoluble in the composition.

Examples 16-19

[0091] Effect of sequesterant type is demonstrated in Table 3 below, in which the sequesterant type was varied in the presence and absence of fatty acid (FA). Cumulative foam volume, ('CFV') is measured in cubic centimetres for a standard initial volume and shaking protocol as described above with reference to examples 3-8. The CFV indicates the total volume of foam generated in the rinsing process, using water of 26 French hardness. Number of rinses required to eliminate the foam was determined as described above.

TABLE 3

	FA	CITRATE	EDTA	CFV	RINSES
Ex. 16	- (Ex. 1)	4%	-	3800	8.5
Ex. 17	0.5 (Ex. 2)	4%	-	3375	5.5
Ex. 18	-	-	4%	3850	7.5
Ex. 19	0.5	-	4%	3400	5.5

[0092] From the above Table 3 it can be seen that better results are obtained with fatty acid and sequesterant present.

Examples 20-26

[0093] Effect of pH is demonstrated with reference to the data presented in Table 4 below. CFV and rinsing measurements were made as mentioned above, using both 12 and 26 French hardness water. Results are generally presented for 26 French water although similar results were obtained with the softer water (Examples 25 and 26). Examples 20, 22 and 23 are comparative examples.

TABLE 4

	FA	pH	CFV	RINSES
Ex. 20	- (Ex. 1)	4.3	3800	8.5
Ex. 21	0.5 (Ex. 2)	4.3	3375	5.5
Ex. 22	-	10.5	3625	9.0
Ex. 23	0.5	10.5	1400	3.0
Ex. 24	0.5	c. 2.5	2325	5.5
Ex. 25	0.5	4.3	3400	6.0
Ex. 26	0.5	c. 2.5	5100	9.0

[0094] The results given above show that in alkaline products the antifoaming effect of the fatty acid is very marked.

However, these alkaline compositions do not effectively remove limescale. Examples 24 and 26 show the effect of omitting the alkaline component (NaOH) of the buffer from the composition. The composition of Example 24 shows similar behaviour to the compositions of the invention in hard water, but is too acidic for use on some surfaces. Examples 25 and 26, with softer water, at 12 French hardness, show that embodiments of the invention (Example 25) exhibit acceptable rinsing whereas in the absence of the alkaline buffer component (Example 26) poor antifoaming is seen.

[0095] It was also noted that the foams generated by compositions at pH around 2.5 had low cling and gave poor cleaning performance.

Examples 27-30

[0096] In examples 27-30, as presented in Table 5, the synergistic inter-relation of solvent and antifoaming fatty acid is shown. Results were obtained as described above.

TABLE 5

	FA	SOLVENT	CFV	RINSES
Ex.27	- (Ex.1)	2%	3800	8.5
Ex.28	0.5 (Ex.2)	2%	3375	5.5
Ex.29	-	-	2325	7.0
Ex.30	0.5	-	2750	7.0

[0097] From the above results it can be seen that the presence of solvent is essential for the fatty acid to exhibit the antifoam effect on dilution. In the absence of solvent (comparative examples 29 and 30), a poor foam was obtained with low cling. In the presence of solvent, foam is stabilised when fatty acid is omitted (comparative example 27). Only in the presence of both fatty acid and solvent are the benefits of a high initial foam volume and rapid rinsing obtained (Example 28).

Examples 31-36

[0098] In examples 31-36, as presented in Table 6, the synergistic effect on product properties of changes in the surfactant system is shown. Results were obtained as described above using 26 French hardness water.

TABLE 6

	FA	ANIONIC	NONIONIC	CFV	RINSES
Ex.31	- (Ex.1)	4%	2%	3800	8.5
Ex.32	0.5 (Ex.2)	4%	2%	3375	5.5
Ex.33	-	-	2%	150	3.0
Ex.34	0.5	-	2%	0	0.0
Ex.35	-	4%	-	4700	7.0
Ex.36	0.5	4%	-	3900	4.5

[0099] Comparative examples 33 and 34 show that in the absence of anionic surfactant little or no foam is generated, allowing the product to run rapidly of sloping surfaces during cleaning operations. Examples 35 and 36 show the effect of the omission of the optional nonionic surfactant in the embodiments of the invention. From comparative example 35 it is seen that non-ionics have some foam suppressing activity although the rinsing time is increased by the presence of nonionics. From these results it is seen that while fatty acid and at least one other anionic are essential components nonionic is optional.

Examples 37-39

[0100] In examples 37-39 given below (see Table 7) the performance of formulations according to the present invention is compared against commercial formulations.

TABLE 7

EXAMPLE	37	38	39
Magnesium PAS	18.5	-	-
PAS (sodium salt)	-	3.5	-
SAS (sodium salt)	-	-	4.0
Nonionic	9.5	-	4.0
Solvent	8.0	-	-
Fatty Acid	0.7	-	-
Isoparaffin	0.75	-	-
Ammonia	1.1	0.75	-
Organic acid	6.0	6.0	6.2
Minors	tr.	tr.	tr.
Water	to 100%	to 100%	to 100%
pH	4.0	acid	acid
Soil/Contact Time			
Kitchen 15s	4	3	2
Fat Soil 15s	3	3	3
30s	3	3	3
60s	4	4	3
Soap Scum 180s	3	1	0
240s	4	2	1

[0101] Table 7 lists two comparative examples (Examples 38 and 39) of current, commercially available acidic bathroom cleaning compositions. These formulations were obtained by analysis. In the composition of example 39 the organic acids were a mixture of succinic, glutaric, adipic and benzoic acids, totalling 6.2wt%. In examples 37 and 38 citric acid was used. It can be seen that the composition of example 38 differs from the present invention in that it does not employ the magnesium salt of PAS and no fatty acid or solvent is present.

[0102] In order to assess the compositions of examples 37-39, soiled tiles were prepared with a coating of a synthetic soap scum, fatty soil and kitchen soil. Each soil comprised a visible trace of carbon black as a visualising agent.

[0103] The soap scum consisted essentially of calcium stearate, applied to a enamelled steel tile by spraying a suspension of calcium stearate in isopropyl alcohol. The tiles were baked at 180 Celcius for 30 minutes after application of the soil.

[0104] The fatty soil consisted of a mixture of fatty acids and paraffin, applied to a ceramic tile by spraying the composition in petroleum ether.

[0105] The kitchen soil consisted of a mixture of fats, fatty acids, paraffin and clay, applied to a ceramic tile by spraying the composition in petroleum ether.

[0106] To assess the effectiveness of the composition 0.5ml of the compositions of examples 37-39 were applied to each of the soiled tiles and left in contact with the tile for the periods specified in Table 7 under 'contact time'. The tile was then mechanically wiped with a clean damp cloth in a single pass at a fixed pressure. The residual soil was assessed visually on a six point scale of 0-5, where 0 indicates no soil removal and 5 indicates complete soil removal as indicated by the removal of the carbon black.

[0107] From the above results it can be seen that the compositions according to the present invention are equivalent to known compositions as regards the fatty soil removal but greatly improved as regards kitchen soil and especially soap scum removal.

Examples 39-43

[0108] In examples 39-44 given below in Table 8, the effect of changes in the ratio of Mg to Na as the counter-ion for the PAS surfactant, at high concentrations, is illustrated. All examples were similar to the formulation of example 37 except that the ratio of Mg:Na PAS was varied.

Table 8

EXAMPLE	MgPAS:NaPAS	
39	10.5:8.0	stable
40	11.0:7.5	stable
41	18.5:0.0	unstable
42	17.7:1.0	unstable
43	15.0:3.5	unstable

[0109] In examples 41-43 Magnesium citrate was found to precipitate out of the product on prolonged storage, while examples 39-40 were storage stable. Products according to examples 41-43 were otherwise acceptable.

Claims

1. Aqueous cleaning composition comprising;

a) 1-40%wt of a surfactant system comprising at least one anionic surfactant other than an alkali metal salt of a fatty acid,

b) 0.1-3%wt a C10-C22 monocarboxylic fatty acid,

c) 1-30%wt of a semi-polar solvent which has dielectric constant of from 5-35

d) 1-10%wt of polycarboxylic acids or salt thereof, and,

e) a base, in an amount sufficient that said composition has a pH of less than the pK_a of the monocarboxylic fatty acid and less than 6.

2. Composition according to claim 1 wherein the semi-polar solvent is selected from; propylene glycol mono n-butyl ether, dipropylene glycol mono n-butyl ether, propylene glycol mono t-butyl ether, dipropylene glycol mono t-butyl ether, diethylene glycol hexyl ether, ethyl acetate, ethanol, isopropyl alcohol, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether and mixtures thereof.

3. Composition according to claim 2 wherein the semi-polar solvent is a glycol ether solvent.

4. Composition according to claim 3 wherein the semi-polar solvent is selected from propylene glycol mono n-butyl

ether and di-ethylene glycol monobutyl ether.

5. Composition according to claim 1 wherein the total surfactant:solvent weight ratio falls in the range 2:1 to 5:1

5 6. Composition according to claim 1 wherein the polycarboxylic acid is selected from the group comprising citric, adipic, succinic, maleic, glutaric acids, salts thereof and mixtures of the acids or salts thereof.

7. Composition according to claim 1 wherein the acidic reserve of the composition is such that the pH exceeds the pK_a of the monocarboxylic acid on addition of more than ten volumes of water having a pH of at least 7.5 are added to one volume of the product.

8. Composition according to claim 7 wherein the acidic reserve of the composition is such that the pH is raised at least above the pK_a of the monocarboxylic acid when less than 1000 volumes of water having a pH of at least 7.5 are added to one volume of the product.

9. Composition according to claim 1 having a pH of from 3.14-4.9.

10. Composition according to claim 1 wherein the at least one anionic surfactant is selected from the group comprising; primary and secondary alcohol sulphates, alcohol ethoxy sulphates, primary and secondary alkane sulphonates, alkylaryl sulphonates and mixtures thereof.

11. Composition according to claim 1 further comprising a non-ionic surfactant.

12. Composition according to claim 11, comprising a surfactant selected from primary alcohol sulphate and alkyl benzene sulphonate together with an alkoxylated alcohol in a weight ratio of from 3:1 to 1:1.

13. Composition according to claim 1 wherein the weight ratio of monocarboxylic acid to anionic surfactant falls into the range 1:4 to 1:20.

14. Compositions according to claim 1 wherein the level of surfactant is 2-10%wt on product.

15. Compositions according to claim 1 wherein the level of surfactant is 20-40%wt on product.

16. Composition according to claim 1 in a package adapted to produce a spray of the product.

17. An acidic aqueous cleaning composition according to claim 1, comprising:

a) 2-40%wt surfactant, said surfactant comprising primary alcohol sulphate and preferably one or more non-ionic surfactant wherein at least 50%wt of the surfactant present is primary alcohol sulphate,

b) 0.2-5%wt C10-18 unbranched fatty acid,

c) at least one solvent selected from the group of glycol ether and 1-5 carbon alcohol solvents, in an amount such that the surfactant:solvent weight ratios fall in the range 1:1 to 10:1,

d) 1-10%wt of a water soluble organic acid, selected from citric, adipic, succinic, glutaric, maleic acids, salts thereof or mixtures thereof, and,

e) sufficient base to bring the pH of the composition into the range 3.14-4.9.

Patentansprüche

1. Wässrige Reinigungszusammensetzung, umfassend:

a) 1-40 Gew.-% eines Tensidsystems, umfassend mindestens ein anionisches Tensid außer einem Alkalimetallsalz einer Fettsäure,

b) 0,1-3 Gew.-% einer C10-C22-Monocarbonsäure,

c) 1-30 Gew.-% eines semipolaren Lösungsmittels, das eine Dielektrizitätskonstante von 5-35 aufweist,

d) 1-10 Gew.-% Polycarbonsäuren oder Salz davon, und

e) eine Base, in einer ausreichenden Menge, damit die Zusammensetzung einen pH-Wert von weniger als den pK_a -Wert der Monocarbonsäure und weniger als 6 aufweist.

- 5 2. Zusammensetzung nach Anspruch 1, wobei das semipolare Lösungsmittel ausgewählt ist aus: Propylenglycolmono-n-butylether, Dipropylenglycolmono-n-butylether, Propylenglycolmono-t-butylether, Dipropylenglycolmono-t-butylether, Diethylenglycolhexylether, Essigsäureethylester, Ethanol, Isopropylalkohol, Ethylenglycolmonobutylether, Diethylenglycolmonobutylether und Gemischen davon.
- 10 3. Zusammensetzung nach Anspruch 2, wobei das semipolare Lösungsmittel ein Glycoetherlösungsmittel darstellt.
4. Zusammensetzung nach Anspruch 3, wobei das semipolare Lösungsmittel ausgewählt ist aus Propylenglycolmono-n-butylether und Diethylenglycolmonobutylether.
- 15 5. Zusammensetzung nach Anspruch 1, wobei das Gewichtsverhältnis von Tensid insgesamt zu Lösungsmittel in den Bereich 2:1 bis 5:1 fällt.
6. Zusammensetzung nach Anspruch 1, wobei die Polycarbonsäure ausgewählt ist aus der Gruppe, umfassend Zitronen-, Adipin-, Bernstein-, Malein-, Glutarsäure, Salze davon und Gemische der Säuren oder Salze davon.
- 20 7. Zusammensetzung nach Anspruch 1, wobei die saure Reserve der Zusammensetzung derart ausgelegt ist, daß der pH-Wert nach Zugabe von mehr als 10 Volumen Wasser mit einem pH-Wert von mindestens 7,5 zu einem Volumen des Produkts den pK_a -Wert der Monocarbonsäure übersteigt.
- 25 8. Zusammensetzung nach Anspruch 7, wobei die saure Reserve der Zusammensetzung derart ausgelegt ist, daß, wenn weniger als 1000 Volumen Wasser mit einem pH-Wert von mindestens 7,5 zu einem Volumen des Produkts gegeben werden, der pH-Wert zumindest über den pK_a -Wert der Monocarbonsäure ansteigt.
9. Zusammensetzung nach Anspruch 1 mit einem pH-Wert von 3,14 bis 4,9.
- 30 10. Zusammensetzung nach Anspruch 1, wobei das mindestens eine anionische Tensid ausgewählt ist aus der Gruppe, umfassend: primäre und sekundäre Alkoholsulfate, Alkoholethoxysulfate, primäre und sekundäre Alkylsulfonate, Alkylarylsulfonate und Gemische davon.
- 35 11. Zusammensetzung nach Anspruch 1, weiterhin ein nichtionisches Tensid umfassend.
12. Zusammensetzung nach Anspruch 11, umfassend ein Tensid, ausgewählt aus primärem Alkoholsulfat und Alkylbenzolsulfonat, zusammen mit einem alkoxylierten Alkohol, in einem Gewichtsverhältnis von 3:1 bis 1:1.
- 40 13. Zusammensetzung nach Anspruch 1, wobei das Gewichtsverhältnis von Monocarbonsäure zu anionischem Tensid in den Bereich 1:4 bis 1:20 fällt.
14. Zusammensetzungen nach Anspruch 1, wobei der Anteil des Tensids 2 bis 10 Gew.-% des Produkts beträgt.
- 45 15. Zusammensetzungen nach Anspruch 1, wobei der Anteil des Tensids 20 bis 40 Gew.-% des Produkts beträgt.
16. Zusammensetzung nach Anspruch 1, in einer Verpackung, ausgelegt zur Erzeugung eines Sprays aus dem Produkt.
- 50 17. Saure, wässrige Reinigungszusammensetzung nach Anspruch 1, umfassend:
 - a) 2 bis 40 Gew.-% Tensid, wobei das Tensid primäres Alkoholsulfat und vorzugsweise ein oder mehrere nicht-ionische Tenside umfaßt, wobei mindestens 50 Gew.-% des vorliegenden Tensids primäres Alkoholsulfat sind,
 - b) 0,2 bis 5 Gew.-% nichtverzweigte C10-C18-Fettsäure,
 - 55 c) mindestens ein Lösungsmittel, ausgewählt aus der Gruppe von Glycoether und Alkohollösungsmitteln mit 1 bis 5 Kohlenstoffatomen, in einer Menge, so daß die Gewichtsverhältnisse von Tensid zu Lösungsmittel in den Bereich 1:1 bis 10:1 fallen,
 - d) 1 bis 10 Gew.-% einer wasserlöslichen organischen Säure, ausgewählt aus Zitronen-, Adipin-, Bernstein-,

Glutar-, Maleinsäure, Salzen davon oder Gemischen davon, und
e) ausreichend Base, um den pH-Wert der Zusammensetzung in den Bereich von 3,14 bis 4,9 zu bringen.

Revendications

- 5 1. Composition de nettoyage aqueuse comprenant:
 - a) 1 à 40% en poids d'un système tensioactif comprenant au moins un tensioactif anionique autre qu'un sel de
 - 10 b) 0,1 à 3% en poids d'un acide gras monocarboxylique en C10-22,
 - c) 1 à 30% en poids d'un solvant semi-polaire qui a une constante diélectrique de 5 à 35,
 - d) 1 à 10% en poids d'acide polycarboxylique ou son sel, et,
 - e) une base, en une quantité suffisante pour que ladite composition ait un pH inférieur au pKa de l'acide gras monocarboxylique et inférieur à 6.
- 15 2. Composition selon la revendication 1, dans laquelle le solvant semi-polaire est choisi parmi les mono-n-butyléther de propylène-glycol, mono-n-butyléther de dipropylène-glycol, mono-t-butyléther de propylène-glycol, mono-t-butyléther de dipropylène-glycol, hexyléther de diéthylène-glycol, acétate d'éthyle, éthanol, alcool isopropylique, mono-butyléther d'éthylène-glycol, monobutyléther de di-éthylène-glycol et leurs mélanges.
- 20 3. Composition selon la revendication 2, dans laquelle le solvant semi-polaire est un solvant éther glycolique.
4. Composition selon la revendication 3, dans laquelle le solvant semi-polaire est choisi parmi le mono-n-butyléther de propylène-glycol et le monobutyléther de di-éthylène-glycol.
- 25 5. Composition selon la revendication 1, dans laquelle le rapport pondéral tensioactif total/solvant est dans la gamme 2:1 à 5:1.
- 30 6. Composition selon la revendication 1, dans laquelle on choisit l'acide polycarboxylique parmi les acides citrique, adipique, succinique, maléique, glutarique, leurs sels et les mélanges des acides ou de leurs sels.
- 35 7. Composition selon la revendication 1, dans laquelle la réserve acide de la composition est telle que le pH excède le pKa de l'acide monocarboxylique lors de l'addition de plus de 10 volumes d'eau ayant un pH d'au moins 7,5 à un volume du produit.
8. Composition selon la revendication 7, dans laquelle la réserve acide de la composition est telle que le pH monte au moins au dessus du pKa de l'acide monocarboxylique quand on ajoute moins 1000 volumes d'eau ayant un pH d'au moins 7,5 à un volume du produit.
- 40 9. Composition selon la revendication 1, ayant un pH de 3,14 à 4,9.
10. Composition selon la revendication 1, dans laquelle on choisit le tensioactif anionique parmi des alcool-sulfates primaires et secondaires, des éthoxysulfates d'alcools, des alcane-sulfonates primaires et secondaires, des alkylaryl-sulfonates et leurs mélanges.
- 45 11. Composition selon la revendication 1, comprenant de plus un tensioactif non ionique.
12. Composition selon la revendication 11, comprenant un tensioactif choisi parmi l'alcool-sulfate primaire et l'alkyl-benzène-sulfonate avec un alcool alcoxylé en un rapport pondéral de 3:1 à 1:1.
- 50 13. Composition selon la revendication 1, dans laquelle le rapport pondéral de l'acide monocarboxylique au tensioactif anionique est dans la gamme 1:4 à 1:20.
14. Composition selon la revendication 1, dans laquelle la quantité de tensioactif est de 2 à 10% en poids par rapport au produit.
- 55 15. Composition selon la revendication 1, dans laquelle la quantité de tensioactif est de 20 à 40% en poids par rapport au produit.

16. Composition selon la revendication 1, dans un emballage adapté pour produire une pulvérisation du produit.

17. Composition de nettoyage aqueuse acide selon la revendication 1, comprenant :

- 5 a) 2 à 40% en poids de tensioactif, ledit tensioactif comprenant un alcool-sulfate primaire et de préférence, un ou plusieurs tensioactifs non ioniques, au moins 50% en poids du tensioactif présent étant un alcool-sulfate primaire,
- b) 0,2 à 5% en poids d'acide gras en C10-18 non ramifié,
- 10 c) au moins un solvant choisi parmi l'éther glycolique et des solvants alcools avec 1 à 5 atomes de carbone, en une quantité telle que les rapports pondéraux tensioactif:solvant sont dans la gamme 1:1 à 10:1.
- d) 1 à 10% en poids d'un acide organique hydrosoluble, choisi parmi les acides citrique, adipique, succinique, glutarique, maléique, leurs sels ou leurs mélanges, et
- e) une base suffisante pour porter le pH de la composition dans la gamme de 3,14 à 4,9.

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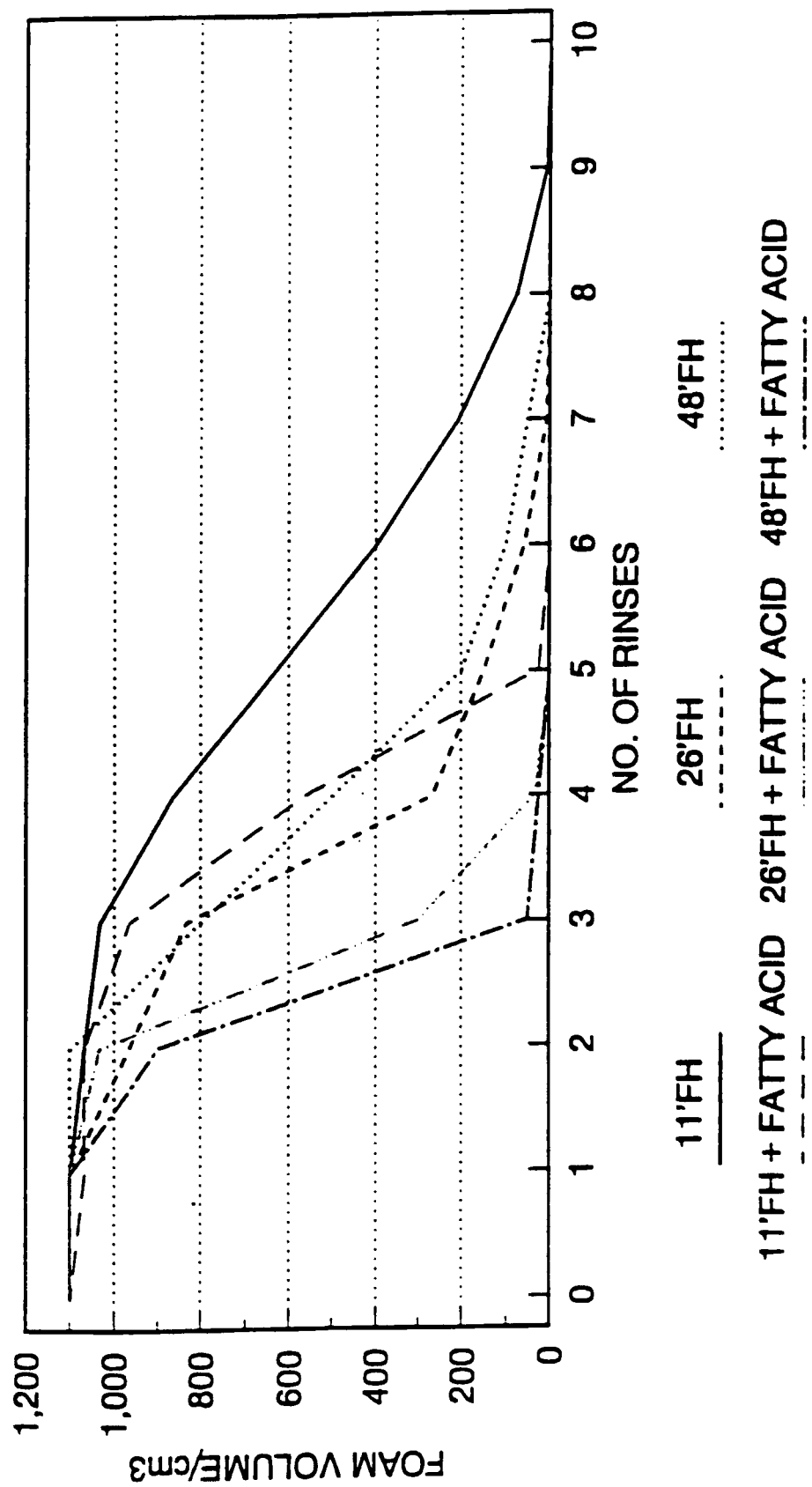
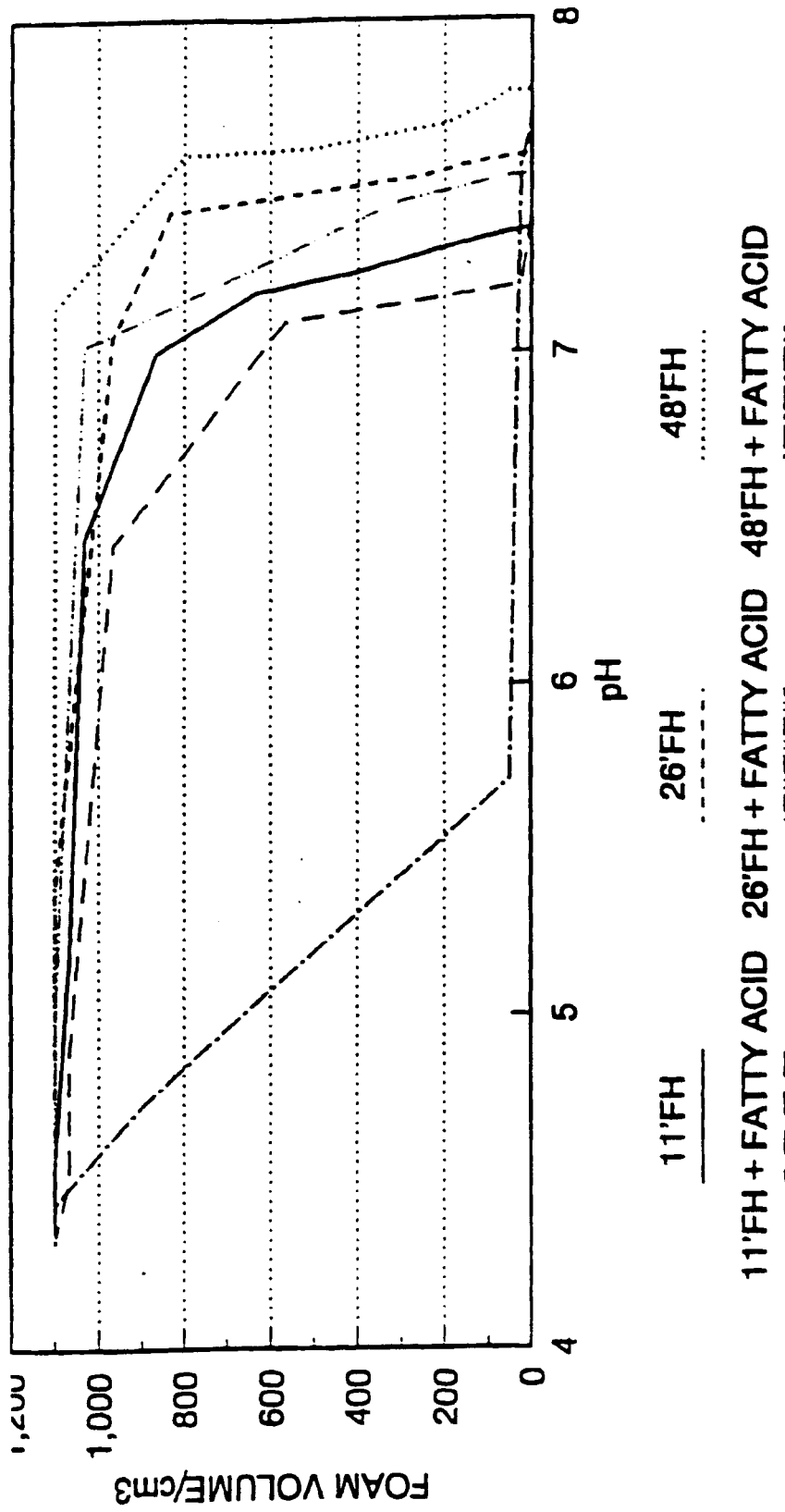


Fig. 1



11'FH = WIRRAL WATER
 26'FH = PRENTON TANK
 48'FH = HAUBOURDIN WATER

Fig. 2