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(54) **Thickening gels.**

(57) Liquid detergent compositions useful for hard surface cleaning and other applications, particularly in industrial applications, comprise surfactant blends such that the compositions undergo a viscosity increase upon aqueous dilution. The invention also extends to a method of spraying a target surface with such a composition after such dilution, e.g. in the form of a foam.

THICKENING GELS

The present invention is concerned with liquid detergent compositions.

For the cleaning of hard surfaces and objects, particularly in industrial, institutional and catering environments, there is a need for detergent products which can be applied over a wide area and which clean upon immediate and/or prolonged contact with the surface to be cleaned, before being removed.

We have now found that this can be achieved by using a liquid detergent composition which undergoes a viscosity increase upon aqueous dilution.

The advantage in such a composition according to the invention is that prior to dilution, it can be a readily mobile liquid which is convenient for transport etc., but when diluted to working concentration, it starts to thicken to a syrupy or gel-like consistency, which means that it will remain in contact with the surface or object to be cleaned, for sufficient time to enable the required cleansing to occur. However, when in the thickened state at working dilution, such compositions are shear thinning, enabling convenient application by suitable means, e.g. a post-pump injector (which can bring about the required dilution of the concentrated product) together with a lance. That enables the diluted product to be sprayed over a wide area; yet it starts to thicken upon contact with the surface or object to be cleaned. Typical working dilutions are from about 5 to about 15% by weight of the composition in water, especially from about 7.5 to about 10%.

Thus, the present invention further comprises a method of diluting a composition of the invention according to any definition or described embodiment herein, with water or an aqueous vehicle, to a concentration at which the viscosity thereof is increased, and applying the composition thus diluted to a target surface. The term "target surface" means a surface of any article, a working surface, or surface (internal or external) of any equipment or any other surface intended to be contacted by said diluted composition.

It is also very desirable to apply the diluted composition in the form of a foam, i.e. gassified with air or any other suitable gas. Conveniently, this may be effected by injecting the air or other gas into a lance or post-pump injector through which the diluted composition is administered. Application in the form of a foam has the advantage of enabling the areas of the surface contacted to be seen better, thus obviating the need for inclusion of a dye for this purpose. It has also been found that in some instances, application as a foam enhances cleaning performance and rinsability.

The rheological behaviour described above in respect of compositions according to the present invention is brought about by use of appropriate surfactant blends. However, in general it can be stated that any category of surfactant described herein for use in compositions of the present invention, for whatever purpose, may be selected from any of the classes, sub-classes and specific materials described in "Surface Active Agents" Vol. I, by Schwartz & Perry, Interscience 1949 "Surface Active Agents" Vol. II, by Schwartz, Perry & Berch, Interscience 1958; in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon Division of Manufacturing Confectioners Company or in "Tensid-Taschenbuch", H.Stache, 2nd Edition,, Carl Hanser Verlag, München & Wien, 1981.

In general, it can be stated that preferred compositions having the required properties may be formulated using

a) primary surfactant material which comprises one or more agents selected from amine, amine oxide, betaine and quaternary ammonium surfactant compounds;

b) co-surfactant material which is a hydrotrope for the primary surfactant material;

c) one or more water-soluble or water-miscible, non-surfactant compounds which are ionisable in water; and

d) water.

Preferably, such compositions comprise from about 0.1 to about 10% by weight of component (a), from about 0.05 to about 5% by weight of component (b) and from about 0.01 to about 30% by weight of component (c), preferably from about 0.5 to about 5% by weight of component (a), from about 0.5 to about 3% by weight of component (b) and from about I to about 25% by weight of component (c).

For maximising the detergency of the product, it is also preferred to include auxillary surfactant material which is other than the materials defined above for components (a) and (b), i.e. not significantly contributing to the required rheological properties. Preferably, such auxillary surfactant material is present from about I to about 10% by weight of the total composition. Most suitable auxillary surfactant materials comprise nonionic or anionic surfactants, most preferably a blend of both.

As primary surfactant materials, most suitable are those surfactants which are capable of forming addition compounds, especially those having a tri- or tetravalent nitrogen atom. Suitable examples of these are amine or amine oxide surfactant materials in which the nitrogen atom is substituted by two independently selected C_{1-4} alkyl or C_{2-4} hydroxyalkyl groups and by a fatty residue having from 12 to 18 carbon atoms.

Most preferably, the fatty residue in such compounds has from 14 to 16 carbon atoms.

In general, it is preferred that the HLB value of the primary surfactant material (averaged for all constituent surfactants therein, proportionally by weight) is from about 8 to about 12, most preferably around 10. The term "HLB value" refers to the figure for hydrophilic lipophilic balance and is well known in the art, for example as described in "Nonionic Surfactants" Vol.I, Schick (Ed), Arnold, London 1967.

It is also preferred that all or part of the primary surfactant material consists of an amine oxide surfactant which has an HLB value from about l4 to about 18, most preferably 16. As co-surfactant component, anionic surfactant compounds are generally preferred. Especially suitable are those selected from :

(i) alkali metal salts of polyalkoxylated alkyl- or arylalkyl-sulphates or -sulphonates, in which the alkyl moiety has from 12 to 16 carbon atoms; and

(ii) alkali metal or alkaline earth metal salts of benzene or naphthalene sulphates or sulphonates which are mono- or polyalkoxylated on the aryl moiety thereof, with a, or a plurality of independently selected, C_{1-4} alkyl groups.

Of the polyalkoxylated co-surfactants compounds (i), those containing from 3 to 7 ethylene oxide groups are normally the most suitable.

The compositions according to the present invention may be formulated over a very wide pH range, from the highly acidic, through the mild acid, substantially neutral, mild and very alkaline. Usually, the acid compositions are most useful where descaling is required, for example the cleaning-in-place of dairy of brewery equipment. The alkaline compositions are most useful where fatty soil is to be emulsified, for example in the food industry.

The highly acidic compositions normally contain from about 15 to about 25% by weight, most preferably from about 18 to about 22% by weight of acidic material selected from one or more organic and/or inorganic acids. Of these, the inorganic mineral acids are the most preferred, for example nitric, sulphuric, hydrochloric and phosphoric acids. The more mildly acidic compositions will normally contain from about 5 to about 15% by weight of acid material, most preferably from about 8 to about 12%.

Substantially neutral compositions of the invention will contain substantially neutral, or perhaps mildly alkaline salts. Suitable neutral salts are alkali metal sulphates, in particular sodium or potassium sulphate. Suitable mildly alkaline salts are alkali metal carbonates or bicarbonates such as sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate or phosphates such as potassium tripolyphosphate or sodium tripolyphosphate, and tetrasodium pyrophosphate or potassium pyrophosphate. Such mildly alkaline material is preferably used together with other neutral salts or in combination with more alkaline compounds. Generally, it is present at about from 1 to about 10% by weight of the total composition, for example to about 5 to about 6%. When used in combination with more alkaline material, for example as described further hereinbelow, the latter is generally present at from about 1 to about 5% by weight of the composition, typically about 3 to about 4%.

Stronger alkaline materials which may be used are, for example, selected from one or more alkali metal hydroxides and/or alkaline salts of alkali metals. Preferred alkali metal hydroxides are sodium hydroxides (caustic soda) and potassium hydroxide (caustic potash). Preferred alkaline salts are sodium metasilicate, trisodium phosphate, and sodium orthosilicate.

In the case of strongly alkaline materials, especially those comprising alkali metal hydroxides, we have found that ferric ion impurities can catalyse the decomposition of any amine oxides present to the corresponding amine, resulting in a deterioration of the thickening effect upon dilution. To counteract this, it has been found preferable to include a chelating agent capable of chelating ferric ions at a pH above 8. Several materials are known to be capable of performing this role, for example alkali metal gluconates, such as sodium gluconate.

The use of the foregoing stronger alkaline materials in combination with mild alkalis has already been described hereinbefore. However, in heavy duty alkali products, these stronger agents are preferably used at from about 10 to about 15% by weight of the total composition, typically around 12.5%. In very heavy duty alkaline products, the amount of such materials is typically from about 20 to about 30% by weight, typically about 22.5 to about 27%, especially around 25%. The acids, neutral salts and alkalis described above are the most preferred forms of component (c) of the composition as defined hereinbefore.

Typical materials herein described for components (a), (b), (c) are frequently used together in other compositions which do not possess the rheological properties presented here as defining the scope of the present invention in its broadest sense. So, for example, two known proprietory liquid bleach products have a weight ratio of components of type (a) to those of type (b) of, respectively, 0.35:l and 1.11:1. The same products have a weight ratio of components of type (a) to those of type (c) of, respectively, l:10 and 1:16.3. A known proprietory vehicle cleaner has, on the other hand, a weight ratio of components of type (a) to type (b) of 4.42:1 and a weight ratio of components of type (a) to type (c) of 1:0.36. In contrast, it is preferred that compositions according to the present invention have a weight ratio of component (a) to component (b) of from 1.25:1 to 4.25:1, and a weight ratio of component (a) to component (c) of from 1:0.5 to 1:9, preferably from 1:1.75 to 1:7.5.

Preferably though, it is preferred that compositions of the present invention contain no more than 7.5% by weight of bleach compounds, and it is especially preferred that they contain substantially no bleach compounds.

Surprisingly, it has also been found that soil removal is greatly enhanced by incorporating one or more agents comprising a fatty acid esterified with a polyethylene glycol, for example where the fatty acid is oleic acid. Such esters are preferably incorporated at from about 1 to about 10% by weight, most preferably from about 2.5 to 7.5% by weight of the total composition.

It will be recalled that the component (b) hereinbefore defined is co-surfactant material capable of acting as a hydrotrope for the primary surfactant material. However, we have also found it particularly advantageous to incorporate a water-miscible, organic solvent, especially one which is a hydrotrope for soaps and surfactants, such as an alkanol, e.g. ethanol or methanol or an appropriate amine such as triethanolamine. Typically, such solvents are incorporated at from about l to about 10% by weight, typically from about 2 to about 7.5% by weight of the total composition.

It was also found to be useful to incorporate a builder in the composition, especially when it is to be used with water having a high degree of hardness. Suitable builders are well known in the art and preferably comprise tripolyphosphate salts of sodium and/or potassium.

Another material which advantageously may be included in compositions according to the present invention comprises one or more suitable enzymes, for example selected from proteolytic and amylolytic enzymes.

It can also be useful to incorporate one or more microbiocides, for example selected from substituted guanidines (e.g. biguanides), halo-phenylalkanols, p-hydroxybenzoic acid esters and their salts, halobisphenols, benzoic acid and its salts, and phenylphenol and derivatives thereof. However, some amine oxide and quaternary ammonium surfactants (which may constitute all or part of the primary surfactant material) themselves have microbiocidal properties. Similarly, some organic peracids (which may constitute all or part of the aforementioned component (c)), may also be microbials (and/or possess bleaching properties).

Other minor components such as dyes, thinners and perfumes may also be included in compositions according to the invention.

The present invention will now be illustrated by way of the following Examples.

EXAMPLES

Example 1

Acid Product	
	% by weight
Ethomeen S12	7.5
Phosphoric Acid (70% Active)	30
Nitric Acid (60% Active)	6
Sodium Xylene Sulphonate (30% Active)	9
Dobanol 45/7	2.5
Water	balance

Example 2

Acid Product	
	% by weight
Aromox T12	5
Empigen OH (25% Active)	5
Dobanol 45/7	3
Nitric Acid (60% Active)	1.5
Phosphoric Acid (70% Active)	20
Sodium Xylene Sulphonate (30% Active)	5
Isopropyl Alcohol	2
Water	balance

Example 3

Light Duty Mild Alkaline Product	
	% by weight
Dobanol 45/7	1
Sodium Carbonate	5.7
Empigen OH (25% Active)	12.4
Aromox T12 (49% Active)	3.7
KSN 27 (27% Active)	3.8
Dodecyl Benzene Sulphonate	2.3
Sodium Metasilicate	2
NaOH	1
EDTA (39% Active)	0.8
Dequest 2000	0.5
Ethanol	5
Sodium Xylene Sulphonate (30% Active)	5.1
Water	balance

Example 4

Medium Duty Alkaline Product	
	% by weight
NaOH Liquor (50% Active)	6
Dequest 2000	0.5
Sodium Gluconate	0.5
Trilon A (40% Active)	9
Dobanol 45/7	0.7
Aromox T12 (49% Active)	10.5
Isopropyl Alcohol	7.6
Wardol X	4
Dobanol 25-3S/27	6.2
Water	balance

Example 5

Heavy Duty Alkaline Product	
	% by weight
Dequest 2000	0.5
EDTA (39% Active)	2
NaOH	12.5
Sodium Xylene Sulphonate (30% Active)	4.3
Wardol X	6
Aromox T12 (49% Active)	8.9
Empigen OH (25% Active)	2
KSN 27 (27% Active)	6
Isopropyl alcohol	3
Water	balance

Example 6

Heavy Duty Alkaline Product	
	% by weight
Dequest 2000	0.5
Trilon A (40% Active)	3
Wardol X	6
Isopropyl Alcohol	2.6
Sodium Gluconate	0.5
Aromox T12 (49% Active)	10
Dobanol 23-3S/27	10
NaOH Liquor (47% Active)	25
Water	balance

Example 7

Very Heavy Duty Alkaline Product	
	% by weight
NaOH	22.5
Aromox T12 (49% Active)	5.5
Empigen OH (25% Active)	2.4
KSN 27 (27% Active)	6
Water	balance

Example 8

Very Heavy Duty Alkaline Product	
	% by weight
Sodium Gluconate	1
Nansa 1042	1
IMS 99	7.5
Aromox T12 (49% Active)	6
Dobanol 23-3S/27	14.5
NaOH Liquor (49% Active)	55
Water	balance

Commercial Materials:

Ethomeen S12	N,N-dihydroxyethyl(oleylamine) (Ex Akzo)
Dobanol 45/7	C_{14-15} fatty alcohol ethoxylated with an average of 7 Moles of ethylene oxide (ex Shell)
Aromox T12	Amine Oxide Surfactant (ex Akzo)
Empigen OH	C_{14} Tertiary Amine Oxide Surfactant (ex Albright & Wilson)
KSN 27	Lauryl Sulphate ethoxylated with an average of 3 Moles of ethylene oxide (ex Albright & Wilson)
Dobanol 23-3S/27	Substantially as KSN 27 (but ex Shell)
Dobanol 25-3S/27	Substantially as KSN 27, but having a C_{12}-C_{15} fatty alcohol chain (ex Shell)
Dequest 2000	Phosphonate sequestrant (ex Monsanto)
Wardol X	Mixture of polyethylene glycol esters of oleic acid (ex Leek Chemicals (ICI))
Trilon A	Trisodium nitrilotriacetate (ex BASF)
Nansa 1042	Dodecyl benzene sulphonic acid (ex Albright & Wilson)

IMS 99	Industrial methylated spirit (ex Hardings)

Claims

1. A liquid detergent composition which undergoes a viscosity increase upon aqueous dilution, comprising

a) primary surfactant material which comprises one or more agents selected from amine, amine oxide, betaine and quaternary ammonium surfactant compounds;

b) co-surfactant material which is a hydrotrope for the primary surfactant material;

c) one or more water-soluble or water-miscible, non-surfactant compounds which are ionisable in water; and

d) water.

2. A composition according to Claim 1, comprising from about 0.1 to about 10% by weight of component (a), from about 0.05 to about 5% by weight of component (b) and from about 0.01 to about 30% by weight of component (c).

3. A composition according to Claim 1 or Claim 2, comprising from about 0.5 to about 5% by weight of component (a), from about 0.5 to about 3% by weight of component (b) and from about l to about 25% by weight of component (c).

4. A composition according to any of Claims 1-3, further comprising from about 1 to about 10% by weight of auxilliary surfactant material which is other than the materials defined for components (a) and (b).

5. A composition according to any of Claims 1-4, wherein the primary surfactant material comprises one or more independently selected amine or amine oxide surfactant materials in which the nitrogen atom is substituted by two independently selected C_{1-4} alkyl or C_{2-4} hydroxyalkyl groups and by a fatty residue having from 12 to 18 carbon atoms.

6. A composition according to any of Claims 1-5, wherein the primary surfactant material has an average HLB value of from about 8 to about 12.

7. A composition according to any of Claims 1-6, wherein the primary surfactant comprises an amine oxide surfactant compound having an HLB value from about 14 to about 18.

8. A composition according to any of Claims 1-7, wherein the co-surfactant comprises one or more anionic surfactant compounds.

9. A composition according to Claim 8, wherein the anionic surfactant compound or compounds, is/are selected from

(i) alkali metal salts of polyalkoxylated alkyl- or arylalkyl-sulphates or -sulphonates, in which the alkyl moiety has from 12 to 16 carbon atoms; and

(ii) alkali metal or alkaline earth metal salts of benzene or naphthalene sulphates or sulphonates, which are mono- or polyalkoxylated on the aryl moiety thereof, with a, or a plurality of independently selected, C_{1-4} alkyl groups.

10. A composition according to Claim 9, wherein the surfactants of group (i) are polyalkoxylated with from 3 to 7 ethylene oxide groups.

11. A composition according to any of Claims 1-10, wherein the component (c) comprises a base and the primary surfactant material is as defined in Claim 7, the compositions further comprising a chelating agent capable of chelating ferric ions at a pH above 8.

12. A composition according to Claim 11, wherein the chelating agent is an alkali metal gluconate.

13. A composition according to any of Claims 1-10, wherein component (c) comprises a substantially neutral or weakly alkaline salt.

14. A composition according to any of Claims 1-13, wherein the weight ratio of component (a) to component (b) is from 1.25:1 to 4.25:1.

15. A composition according to any of Claims 1-14, wherein the weight ratio of component (a) to component (c) is from 1:1.75 to 1:7.5.

16. A method comprising diluting a composition according to any preceding Claim, with water or an aqueous vehicle, to a concentration at which the viscosity thereof is increased, and applying the composition thus diluted to a target surface.

17. A method according to Claim 16, in which the diluted composition is applied to the target surface in the form of a foam.