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(54) **LIQUID CLEANING PRODUCTS.**

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**EP-A- 0 385 521**
**FR-A- 2 393 846**
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## Description

The present invention relates to non-aqueous liquid cleaning products, especially non-aqueous liquid detergent compositions containing particulate solid materials dispersed in a liquid phase. Non-aqueous liquids are those containing little or no water.

Non-aqueous liquid cleaning products often comprise a liquid phase comprising a nonionic surfactant material. Generally these nonionic surfactant materials have as one of their main functions to clean objects such as fabrics to be washed or hard surfaces. These detergency nonionics often comprise a fatty alcohol chain comprising from 9 to 15 carbon atoms, said chain being alkoxylated with on average more than 5 alkoxy groups such as ethoxy or propoxy groups or mixtures thereof.

A problem in using detergency nonionics in non-aqueous liquid detergent compositions is that they often generate high foam levels, specifically in the rinsing spinning cycles of washing machines. One way of reducing the amount of foam is to incorporate foam control agents such as silicone-materials. For adequately reducing the foam-problem, hitherto it proved sometimes necessary to use relatively high levels of costly silicone anti-foam materials. Therefore there still exists a need for foam-control materials other than silicone anti-foam materials.

Another problem in using detergency nonionics is sometimes the occurence of relatively high viscosities of the final product, especially at a relatively low temperature, for example 5 °C.

Another problem with non-aqueous liquid detergent products is sometimes the occurance of off-odours caused by the use of certain surfactant materials.

GB-A-2,011,942 describes aqueous liquid detergent compositions comprising a specific ternary nonionic mixture. FR-A-2,393,846 and EP-0,158,464 describe non-aqueous liquid detergents that may comprise alkoxylated nonionic mixtures.

Surprisingly it has now been found that the above described foam formation and/or the viscosity problem and/or the occurance of off-odours can be reduced by incorporating in the liquid detergent composition a specific mixture of nonionic surfactant ingredients.

Especially it has been found that mixtures of relatively hydrophilic alkoxylated detergency nonionics and relatively hydrophobic nonionic ingredients having a relatively small hydrophilic headgroup are suitable for this purpose.

Preferred relatively hydrophilic alkoxylated detergency nonionics are selected from the group consisting of alkoxylated fatty alcohols, said alcohol comprising on average more than 9 and less than 12 carbon atoms and being alkoxylated with on average more than 5 and less than 10 alkoxy-groups selected from ethoxy and/or propoxy groups.

Preferred relatively hydrophobic nonionic ingredients do not have as their main function a detergency function if used in the absence of other detergency materials, therefore they are referred to as nonionic non-detergency ingredients. Especially preferred non-detergency materials for use in compositions of the invention are nonionic ingredients which are selected from the groups of alkoxylated fatty alcohols, said alcohol comprising on average 12 to 16 carbon atoms and being alkoxylated with on average less than 5 alkoxy groups selected from ethoxy and/or propoxy groups and fatty alcohols having a carbon chain length of from 9 to 15.

Further possible advantages of the invention are increased cleaning properties especially on oily soil and reduced costs of production.

Accordingly the present invention relates to a liquid non-aqueous detergent composition comprising nonionic surfactant, characterised in that the nonionic surfactant is a mixture of:

(a) one or more detergency nonionic materials selected from the group consisting of alkoxylated fatty alcohols, said alcohol comprising on average more than 9 and less than 12 carbon atoms and being alkoxylated with on average more than 5 and less than 10 alkoxy-groups selected from ethoxy and/or propoxy groups; and

(b) one or more nonionic non-detergency ingredients, which are selected from the groups of alkoxylated fatty alcohols, said alcohol comprising on average from 12 to 16 carbon atoms and being alkoxylated with on average less than 5 alkoxy groups selected from ethoxy and/or propoxy groups and fatty alcohols having a carbon chain length of from 9 to 15.

For the purpose of the present invention a distinction between detergency nonionic materials and nonionic non-detergency ingredients can be made by applying the following test: Six soiled test-cloths ( 2 x WFK 10C, 2 x WFK 20C and 2 x WFK 30C) are washed in a tergotometer at 40 °C for 15 minutes at 75 rpm in water of 24 °FH. The weight ratio of cloth to water is 1 : 40. The water contains 1.25 g/l of nonionic material and a buffering system of 0.15 g/l borax and 0.10 g/l of triethanolamine. After washing, the cloths are centrifuged and dried, whereafter the reflectometer-score for the WFK 20 C cloths is measured in an Elrepho reflectometer at 460 nm. Detergency nonionic materials will generally provide a reflectometer-score of more than 3.5, more

preferred more than 4.0, most preferred more than 4.5. Nonionic non-detergency ingredients will generally provide a reflectometerscore of less than 3.5, more preferred less than 2.5, most preferred less than 1.5.

The detergency nonionic material

Compositions of the invention comprise one or more detergency nonionic materials selected from the group consisting of alkoxylated fatty alcohols having on average more than 9 and less than 12 carbon atoms and being alkoxylated with on average more than 5 and less than 10 alkoxy-groups selected from ethoxy and/or propoxy groups.

Preferably these nonionic materials additionally satisfy one or more of the following conditions:

(a) the material has an HLB value of more than 12, preferably from 12.5 to 14;

(b) the material has a conductivity of more than $10 \times 10^{-4}$ $ohm^{-1}$ $m^{-1}$;

(c) the material has a standard foam height of more than 40 mm.

As far as condition (a) is concerned, the HLB value (the hydrophilic-lipophilic balance) is a well-known parameter for determining the hydrophilic character of nonionic ingredients. A higher HLB value indicates a more hydrophilic character of the nonionic material. A preferred method for calculating the HLB of a material is to divide the average molecular weight of the hydrophilic portion of the molecule times 20, by the average molecular weight of the whole molecule. This method is especially suitable for calculating the HLB of ethoxylated fatty alcohols. For detergency purposes it is preferred that the HLB value of the detergency nonionic material is 12 or more, preferably from 12.5 to 14.

The conductivity of condition (b) is determined in accordance with the following method: the detergency nonionic material is mixed with Na Dobs in a weight ratio of 50 : 1 and the conductivity of the mixture is measured with a Hewlett Packard Impedantie-meter 4800A. Preferably the conductivity of the mixture is more than $1 \times 10^{-4}$ $ohm^{-1}$ $m^{-1}$, more preferred between $1.5 \times 10^{-4}$ and $2.5 \times 10^{-4}$ $ohm^{-1}$ $m^{-1}$.

The foam height in accordance with test (c) is determined in accordance with the following method: 250 ml of water of 16 °FH is mixed with 0.125 g of the detergency nonionic, the solution is stirred vigorously for 40 seconds in a pipe of 6.5 cm diameter and the foam height is determined. Preferably the height of the developed foam is more than 40 mm, more preferred more than 45 mm, most preferably between 50 and 100 mm.

Nonionic detergency materials as specified above preferably additionally satisfy one or more of the above conditions. It is preferred that test (a), eventually in combination with tests (b) and/or (c) are satisfied.

A very preferred embodiment of the invention concerns the use of so-called narrow range ethoxylates as detergency nonionic materials. Examples of these materials are disclosed in our non-prepublished patent application EP 90200283.1 (published as EP 385 521). Preferably the detergency nonionic is an ethoxylated alcohol having an average of from 5 to 8 ethylene oxide (EO) groups per molecule, at least 60% having a number of ethylene oxide groups within ±2EO of the average and the alkyl chain distribution being such that less than 2% has a chain length of 9 or less carbon atoms, at least 90% has a chain length between 10 and 12 carbon atoms and less than 10% has a chain length of 13 or more carbon atoms, said percentages being by weight of the ethoxylated alcohol. Preferred narrow range ethoxylates are available from Vista.

The use of these nonionic materials is particularly preferred for the prevention of off-odours.

Also prefered is the use of C10-12 alcohols ethoxylated with on average 6-10 ethoxy groups.

The detergency nonionic material preferably is liquid at 20 °C and preferably has a pour point of less than 10 °C, more preferably less than 5 °C.

The level of the detergency nonionic material is preferably from 5 to 75 % by weight of the composition, more preferably from 10 to 40 %, most preferably from 25 to 35 %.

The nonionic non-detergency ingredient

The nonionic non-detergency ingredient is used in compositions of the invention as a foam control agent and/or viscosity control agent and/or for the prevention of off-odours. This means that preferably these materials should be able to reduce the amount of foaming of the compositions when used in a washing machine and/or to reduce the viscosity of the product and/or they should not give rise to off-odours.

Suitable nonionic non-detergency materials are selected from the groups of alkoxylated fatty alcohols comprising on average from 12 to 16 carbon atoms and being alkoxylated with on average less than 5 alkoxy groups selected from ethoxy and/or propoxy groups and fatty alcohols having a carbon chain length of from 9 to 15.

Preferably C 13-15 alcohols ethoxylated with on average 2-4 ethoxy groups are used. Most prefered is the use of a C 13-15 alcohol ethoxylated with on average about 3 ethoxy groups.

It has been found that suitable non-detergency nonionic ingredients preferably additionally satisfy one or

more of the following tests:

(a) the ingredient has an HLB value of less than 12, preferably from 4 to 11, most preferably from 5 to 10;

(b) the ingredient provides a standard conductivity reduction of at least 10%.

(c) the ingredient provides a standard foam height reduction of at least 30%.

(d) the ingredient provides a standard viscosity reduction of at least 100 mPa.s at 21 $s^{-1}$.

With respect to test (a), preferably the HLB value of the nonionic non-detergency ingredient is less than 12, more preferably from 4-11, most preferably from 5-10. Preferably narrow range ethoxylates are used.

According to test (b), the nonionic non-detergency ingredient preferably is capable to reduce the conductivity of a standard solution. The reduction of conductivity can be measured as follows: a mixture is made of the nonionic non-detergency ingredient, a nonionic material having the trade name Dobanol 91-6 and Na Dobs in weight ratios of 15 : 35 : 1. The conductivity of this mixture should be less than the conductivity of a 50 : 1 mixture of Dobanol 91-6 and Na Dobs. Preferably the reduction in conductivity is at least 10%, more preferred more than 30%, most preferred more than 50%.

Condition (c) can be tested as follows: 250 ml of water of 16 °FH is mixed with 0.125 g of a 1 : 1 (by weight) mixture of Dobanol 91-6 and the nonionic non-detergency ingredient, the solution is vigorously stirred for 40 seconds in a pipe of 6.5 cm diameter. The foam height is determined. Preferably the height of the developed foam is at least 30% less than the amount of foam generated when 0.125 g of pure Dobanol 91-6 is used, more preferably the foam reduction is at least 50%, most preferably from 70 to 100%.

Condition (d) can be tested by measuring the viscosity at $21s^{-1}$ of the following composition:

| | |
|---|---|
| Nonionic | 45 % |
| GTA | 5 % |
| ABSA | 5 % |
| Na-carbonate | 20 % |
| Calcite | 8 % |
| perborate.mono | 12 % |
| TAED | 5 % |

For reference the nonionic is Dobanol 91-6, for determining the standard viscosity reduction the Nonionic is a 2 : 1 (by weight) mixture of Dobanol 91-6 and the nonionic non-detergency ingredient. Preferably the viscosity reduction by substituting the Dobanol 91-6 by the mixture of nonionic materials is at least 100 mPa.s, more preferred more than 250 mPa.s, most preferred more than 500 mPa.s at 21 $s^{-1}$.

Preferably the nonionic non-detergency ingredient is liquid at 20 °C. Also preferably the pour point of the ingredient is les than 10 °C, more preferably less than 5 °C.

The level of the nonionic non-detergency ingredient is preferably from 1 to 30 % by weight of the composition, more preferably from 3 to 20 %, most preferably from 7 to 17 %.

The weight ratio of detergency nonionic material to nonionic non-detergency ingredient is preferably from 10 : 1 to 1 : 5, more preferably from 5 : 1 to 1 : 3, most preferably from 4 : 1 to 1 : 1.

## PRODUCT FORM

All compositions according to the present invention are non-aqueous liquid cleaning products. In the context of this specification, all references to liquids refer to materials which are liquid at 25°C at atmospheric pressure. They may be formulated in a very wide range of specific forms, according to the intended use. They may be formulated as cleaners for hard surfaces (with or without abrasive) or as agents for warewashing (cleaning of dishes, cutlery etc) either by hand or mechanical means, as well as in the form of specialised cleaning products, such as for surgical apparatus or artificial dentures. They may also be formulated as agents for washing and/or conditioning of fabrics.

Composition according to the invention will contain a detergency nonionic material. In addition thereto, the compositions may contain one or more agents which further promote the cleaning and/or conditioning of the article(s) in question, selected according to the intended application. Usually, these agents will be selected from surfactants, enzymes, bleaches, microbiocides, (for fabrics) fabric softening agents and (in the case of hard surface cleaning) abrasives. Of course in many cases, more than one of these agents will be present, as well as other ingredients commonly used in the relevant product form.

## SURFACTANT

Where surfactants are solids, they will usually be dissolved or dispersed in the liquid phase. Where they are liquids, they will usually constitute all or part of the liquid phase. However, in some cases the surfactants may undergo a phase change in the composition.

In general, surfactants for use in the compositions of the invention may be chosen from any of the classes, sub-classes and specific materials described in "Surface Active Agents" Vol. I, by Schwartz & Perry, Interscience 1949 and "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 Edn., Carl Hanser Verlag, München & Wien, 1981.

In respect of all surfactant materials, but also with reference to all ingredients described herein as examples of components in compositions according to the present invention, unless the context requires otherwise, the term "alkyl" refers to a straight or branched alkyl moiety having from 1 to 30 carbon atoms, whereas lower alkyl refers to a straight or branched alkyl moiety of from 1 to 4 carbon atoms. These definitions apply to alkyl species however incorporated (e.g. as part of an aralkyl species). Alkenyl (olefin) and alkynyl (acetylene) species are to be interpreted likewise (i.e. in terms of configuration and number of carbon atoms) as are equivalent alkylene, alkenylene and alkynylene linkages. For the avoidance of doubt, any reference to lower alkyl or $C_{1-4}$ alkyl (unless the context so forbids) is to be taken specifically as a recitation of each species wherein the alkyl group is (independent of any other alkyl group which may be present in the same molecule) methyl, ethyl, iso-propyl, n-propyl, n-butyl, iso-butyl and t-butyl, and lower (or $C_{1-4}$) alkylene is to be construed likewise.

All ingredients before incorporation will either be liquid, in which case, in the composition they will constitute all or part of the liquid phase, or they will be solids, in which case, in the composition they will either be dispersed in the liquid phase or they will be dissolved therein. Thus as used herein, the term "solids" is to be construed as referring to materials in the solid phase which are added to the composition and are dispersed therein in solid form, those solids which dissolve in the liquid phase and those in the liquid phase which solidify (undergo a phase change) in the composition, wherein they are then dispersed.

## ANIONIC SURFACTANTS

Examples of suitable anionic detergent surfactants are alkali metal, ammonium or alkylolamine salts of alkylbenzene sulphonates having from 10 to 18 carbon atoms in the alkyl group, alkyl and alkylether sulphates having from 10 to 24 carbon atoms in the alkyl group, the alkylether sulphates having from 1 to 5 ethylene oxide groups, and olefin sulphonates prepared by sulphonation of $C_{10-24}$ alpha-olefins and subsequent neutralization and hydrolysis of the sulphonation reaction product.

## LEVEL OF LIOUID PHASE

Preferably, the compositions of the invention contain the liquid phase (whether or not comprising liquid surfactant) in an amount of at least 10% by weight of the total composition. The amount of the liquid phase present in the composition may be as high as about 90%, but in most cases the practical amount will lie between 20 and 70% and preferably between 35 and 50% by weight of the composition.

Preferably at least 50 % by weight of the liquid phase is composed of the detergency nonionic material and the nonionic non-detergency ingredient. More preferably at least 70 % of the liquid phase is composed of these two ingredients, most preferably from 80 to 100 %.

## SOLIDS CONTENT

In general, the solids content of the product may be within a very wide range, for example from 10-90%, usually from 30-80% and preferably from 50-65% by weight of the final composition. The solid phase should preferably be in particulate form and preferably have a weight average particle size of less than 300 microns, preferably less than 200 microns, more preferably less than 100 microns, especially less than 10 microns. The particle size may even be of sub-micron size. The proper particle size can be obtained by using materials of the appropriate size or by milling the total product in a suitable milling apparatus. In order to control aggregation of the solid phase leading to unredispersible settling or setting of the composition, it is preferred to include a deflocculant therein.

## OTHER INGREDIENTS

In addition to the components already discussed, there are very many other ingredients which can be incorporated in liquid cleaning products.

There is a very great range of such other ingredients and these will be choosen according to the intended

use of the product. However, the greatest diversity is found in products for fabrics washing and/or conditioning. Many ingredients intended for that purpose will also find application in products for other applications (e.g. in hard surface cleaners and warewashing liquids).

## HYDROPHOBICALLY MODIFIED MATERIALS

The physical stability of non-aqueous liquid detergent compositions can be improved and/or setting problems can be minimised, if hydrophobically modified (HM) dispersants are used.

For the purpose of the present invention, a dispersant material is a material, of which the main purpose is to stabilise the composition. Hydrophobically modified dispersant materials are particulate materials, of which the outer surface has chemically been treated to reduce the hydrophilic nature thereof.

Preferred HM materials have a weight average particle size of from 0.005 to 5 micrometer, more preferred 0.01 to 3 micrometer, most preferred from 0.02 to 0.5 micrometer. The level of the HM material is preferably from 0.1 to 10 % by weight of the composition, more preferred 0.3 to 5 %, most preferred from 0.5 to 3 %.

Preferably the number of hydroxy- and/or acid- groups at the surface of the particles is reduced by the hydrophobing treatment. Suitable reactions include esterification or etherfication of the hydrophilic groups. Preferably the hydrophobing treatment involves at least 10 % of the hydrophilic groups at the surface of the particle, more preferably from 40 to 95 %, most preferably from 50 to 90 %. Partial hydrophobing is preferred over complete hydrophobation.

Preferably HM silica containing dispersants are used. The hydrophobation of the silica particles preferably involves the substitution of the free hydroxy-groups at the outer surface of the silica particles by a short alkyl group. More preferably the surface hydroxy-groups are substituted by methyl groups.

## METAL OXIDES

For reducing the clear layer separation of liquid detergent compositions of the invention, surprisingly it has been found that the combined use of HM particles and particulate metal oxides is especially advantageous. Preferred suspended metal oxides have a bulk density of 200 to 1,000 g/l, more preferred 250 to 800 g/l, especially preferably 300 to 700 g/l, most preferably from 400 to 650 g/l.

Preferably the metal oxide is selected from calcium oxide, magnesium oxide and aluminium oxide, most preferably magnesium oxide is used.

The weight average particle size of the metal oxide is preferably from 0.1 to 200 micrometer, more preferably from 0.5 to 100 micrometer, most preferred from 2 to 70 micrometer. The level of metal oxide is preferably from 0.1 to 7 % by weight of the composition, more preferred from 0.5 to 5 %, most preferred from 1 to 4 %.

## DETERGENCY BUILDERS

The detergency builders are those materials which counteract the effects of calcium, or other ion, water hardness, either by precipitation or by an ion sequestering effect. They comprise both inorganic and organic builders. They may also be sub-divided into the phosphorus-containing and non-phosphorus types, the latter being preferred when environmental considerations are important.

In general, the inorganic builders comprise the various phosphate-, carbonate-, silicate-, borate- and aluminosilicates-type materials, particularly the alkali-metal salt forms. Mixtures of these may also be used.

Examples of phosphorus-containing inorganic builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal carbonates, bicarbonates, borates, silicates, metasilicates, and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic builders include the alkali metal, ammonium and substituted ammonium, citrates, succinates, malonates, fatty acid sulphonates, carboxymethoxy succinates, ammonium polyacetates, carboxylates, polycarboxylates, aminopolycarboxylates, polyacetyl carboxylates and polyhydroxsulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those sold by Monsanto

under the tradename of the Dequest range and alkanehydroxy phosphonates.

Other suitable organic builders include the higher molecular weight polymers and co-polymers known to have builder properties, for example appropriate polyacrylic acid, polymaleic acid and polyacrylic/ polymaleic acid co-polymers and their salts, such as those sold by BASF under the Sokalan Trade Mark.

The level of builder materials is preferably from 5-60 % by weight of the composition, more preferred 10-50 % by weight, most preferred 20-40 %.

## THE DEFLOCCULANT

Preferably compositions of the invention also comprise a deflocculant material. In principle, any material may be used as a deflocculant provided it fulfils the deflocculation test described in European Patent Specification EP-A-266199 (Unilever). The capability of a substance to act as a deflocculant will partly depend on the solids/liquid phase combination. However, especially preferred are acids.

Some typical examples of deflocculants include the alkanoic acids such as acetic, propionic and stearic and their halogenated counterparts such as trichloracetic and trifluoracetic as well as the alkyl (e.g. methane) sulphonic acids and aralkyl (e.g. paratoluene) sulphonic acids.

Examples of suitable inorganic mineral acids and their salts are hydrochloric, carbonic, sulphurous, sulphuric and phosphoric acids; potassium monohydrogen sulphate, sodium monohydrogen sulphate, potassium monohydrogen phosphate, potassium dihydrogen phosphate, sodium monohydrogen phosphate, potassium dihydrogen pyrophosphate, tetrasodium monohydrogen triphosphate.

Other organic acids may also be used as deflocculants, for example formic, lactic, amino acetic, benzoic, salicylic, phthalic, nicotinic, ascorbic, ethylenediamine tetraacetic, and aminophosphonic acids, as well as longer chain fatty carboxylates and triglycerides, such as oleic, stearic, lauric acid and the like. Peracids such as percarboxylic and persulphonic acids may also be used.

The class of acid deflocculants further extends to the Lewis acids, including the anhydrides of inorganic and organic acids. Examples of these are acetic anhydride, maleic anhydride, phthalic anhydride and succinic anhydride, sulphur-trioxide, diphosphorous pentoxide, boron trifluoride, antimony pentachloride.

"Fatty" anions are very suitable deflocculants, and a particularly preferred class of deflocculants comprises anionic surfactants. Although anionics which are salts of alkali or other metals may be used, particularly preferred are the free acid forms of these surfactants (wherein the metal cation is replaced by an $H^+$ cation, i.e. proton). These anionic surfactants include all those classes, sub-classes and specific forms described in the aforementioned general references on surfactants, viz, Schwartz & Perry, Schwartz Perry and Berch, McCutcheon's, Tensid-Taschenbuch; and the free acid forms thereof. Many anionic surfactants have already been described hereinbefore. In the role of deflocculants, the free acid forms of these are generally preferred.

In particular, some preferred sub-classes and examples are the $C_{10}$-$C_{22}$ fatty acids and dimers thereof, the $C_8$-$C_{18}$ alkylbenzene sulphonic acids, the $C_{10}$-$C_{18}$ alkyl- or alkylether sulphuric acid monoesters, the $C_{12}$-$C_{18}$ paraffin sulphonic acids, the fatty acid sulphonic acids, the benzene-, toluene-, xylene- and cumene sulphonic acids and so on. Particularly are the linear $C_{12}$-$C_{18}$ alkylbenzene sulphonic acids.

As well as anionic surfactants, zwitterionic-types can also be used as deflocculants. These may be any described in the aforementioned general surfactant references. One example is lecithin.

The level of the deflocculant material in the composition can be optimised by the means described in the aforementioned EP-A-266199, but in very many cases is at least 0.01%, usually 0.1% and preferably at least 1% by weight, and may be as high as 15% by weight. For most practical purposes, the amount ranges from 2-12%, preferably from 4-10% by weight, based on the final composition.

## THE BLEACH SYSTEM

Preferably compositions of the invention contain one or more bleach ingredients. Bleaches include the halogen, particularly chlorine bleaches such as are provided in the form of alkalimetal hypohalites, e.g. hypochlorites. In the application of fabrics washing, the oxygen bleaches are preferred, for example in the form of an inorganic persalt, preferably with a bleach precursor, or as a peroxy acid compound.

In the case of the inorganic persalt bleaches, the activator makes the bleaching more effective at lower temperatures, i.e. in the range from ambient temperature to about 60°C, so that such bleach systems are commonly known as low-temperature bleach systems and are well-known in the art. The inorganic persalt such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the activator is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than the peroxybleach compound alone. The ratio by weight of the peroxybleach compound to the activator is from

about 20:1 to about 2:1, preferably from about 10:1 to about 3.5:1. Whilst the amount of the bleach system, i.e. peroxybleach compound and activator, may be varied between about 5% and about 35% by weight of the total liquid, it is preferred to use from about 6% to about 30% of the ingredients forming the bleach system. Thus, the preferred level of the peroxybleach compound in the composition is between about 5.5% and about 27% by weight, while the preferred level of the activator is between about 0.5% and about 14%, most preferably between about 1% and about 10% by weight.

Typical examples of the suitable peroxybleach compounds are alkalimetal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persilicates and perphosphates, of which sodium perborate is preferred.

It is particularly preferred to include in the compositions, a stabiliser for the bleach or bleach system, for example ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate or other appropriate organic phosphonate or salt thereof, such as the Dequest range hereinbefore described. These stabilisers can be used in acid or salt form, such as the calcium, magnesium, zinc or aluminium salt form. The stabiliser may be present at a level of up to about 2% by weight, preferably between about 0.1% and about 1.0 % by weight.

The applicants have also found that liquid bleach precursors, such as glycerol triacetate and ethylidene heptanoate acetate, isopropenyl acetate and the like, also function suitably as a material for the liquid phase, thus obviating or reducing any need of additional relatively volatile solvents, such as the lower alkanols, paraffins, glycols and glycolethers and the like,. e.g. for viscosity control.

## MISCELLANEOUS OTHER INGREDIENTS

Other ingredients comprise those remaining ingredients which may be used in liquid cleaning products, such as fabric conditioning agents, enzymes, perfumes (including deoperfumes), micro-biocides, colouring agents, fluorescers, soil-suspending agents (anti-redeposition agents), corrosion inhibitors, enzyme stabilising agents, and lather depressants.

Amongst the fabric conditioning agents which may be used, either in fabric washing liquids or in rinse conditioners, are fabric softening materials such as fabric softening clays, quaternary ammonium salts, imidazolinium salts, fatty amines and cellulases.

Enzymes which can be used in liquids according to the present invention include proteolytic enzymes, amylolytic enzymes and lipolytic enzymes (lipases). Various types of proteolytic enzymes and amylolytic enzymes are known in the art and are commercially available. They may be incorporated as "prills", "marumes" or suspensions e.g.

The fluorescent agents which can be used in the liquid cleaning products according to the invention are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in a detergent composition is generally from 0.02-2% by weight.

When it is desired to include anti-redeposition agents in the liquid cleaning products, the amount thereof is normally from about 0.1% to about 5% by weight, preferably from about 0.2% to about 2.5% by weight of the total liquid composition. Preferred anti-redeposition agents include carboxy derivatives of sugars and celluloses, e.g. sodium carboxymethyl cellulose, anionic poly-electrolytes, especially polymeric aliphatic carboxylates, or organic phosphonates.

## WATER LEVEL

The compositions are substantially non-aqueous, i.e. they contain little or no free water, preferably no more than 5%, preferably less than 3%, especially less than 1% by weight of the total composition. It has been found that the higher the water content, the more likely it is for the viscosity to be too high, or even for setting to occur.

### Preferred composition

Altogether preferred compositions in accordance with the invention comprise:

(a) at least 10 % by weight of a liquid phase, at least 50 % by weight thereof, preferably from 80 to 100 % by weight thereof being a mixture of a detergency nonionic material and a nonionic non-detergency ingredient;

(b) 10 - 90 % by weight of suspended solids;

(c) 0.1 - 15 % by weight of a deflocculant material;

(d) 5.5 - 27 % by weight of a peroxy bleach compound;

(e) 0.5 - 14 % by weight of a bleach activator.

The viscosity of the product is preferably less than 2,500 mPa.s at 21 $s^{-1}$, more preferred less than 2,000, most preferred from 500 to 1,500 mPa.s. Compositions of the invention preferably are free from nonionic materials containing propoxy groups.

USE

Composition in accordance with the present invention may be used for several detergency purposes, for example the cleaning of surfaces and the washing of fabrics. For the washing of fabrics, preferably an aqueous liquor containing 0.1 to 10 %, more preferably 0.2 to 2% of the non-aqueous detergent composition of the invention is used.

PROCESSING

During manufacture, it is preferred that all raw materials should be dry and (in the case of hydratable salts) in a low hydration state, e.g. anhydrous phosphate builder, sodium perborate monohydrate and dry calcite abrasive, where these are employed in the composition. In a preferred process, the dry, substantially anhydrous solids are blended with the liquid phase in a dry vessel. If deflocculant materials are used, these should preferably -at least partly- be mixed with the liquid phase, prior to the addition of the solids. In order to minimise the rate of sedimentation of the solids, this blend is passed through a grinding mill or a combination of mills, e.g. a colloid mill, a corundum disc mill, a horizontal or vertical agitated ball mill, to achieve a particle size of 0.1 to 100 microns, preferably 0.5 to 50 microns, ideally 1 to 10 microns. A preferred combination of such mills is a colloid mill followed by a horizontal ball mill since these can be operated under the conditions required to provide a narrow size distribution in the final product. Of course particulate material already having the desired particle size need not be subjected to this procedure and if desired, can be incorporated during a later stage of processing.

During this milling procedure, the energy input results in a temperature rise in the product and the liberation of air entrapped in or between the particles of the solid ingredients. It is therefore highly desirable to mix any heat sensitive ingredients into the product after the milling stage and a subsequent cooling step. It may also be desirable to de-aerate the product before addition of these (usually minor) ingredients and optionally, at any other stage of the process. Typical ingredients which might be added at this stage are perfumes and enzymes, but might also include highly temperature sensitive bleach components or volatile solvent components which may be desirable in the final composition. However, it is especially preferred that volatile material be introduced after any step of de-aeration. Suitable equipment for cooling (e.g. heat exchangers) and de-aeration will be known to those skilled in the art.

It follows that all equipment used in this process should preferably be completely dry, special care being taken after any cleaning operations. The same is true for subsequent storage and packing equipment.

Example 1

The following compositions (percent by weight) were prepared by mixing the ingredients in the order stated. The ingredients were milled after mixing to give a mean particle size of 5 μm.

| EXAMPLE NO: | I |
|---|---|
| Nonionic[3] | 29.4 |
| Nonionic[4] | 14 |
| Glyceroltriacetate | 5 |
| ABSA[5] | 6 |
| Na carbonate | 18 |
| Calcite | 8 |
| Na perborate monohydrate | 10.5 |
| TAED | 3 |
| Mg oxide[2]) | 1 |
| Sipernat D 17[1])® | 2 |
| Tinopal DMS-X | 0.3 |
| Silicones DB 100 | 0.8 |
| Enzymes (Savinase®/Lipolase®) | 0.7 |
| Perfume | balance |

1 - Hydrophobically modified silica

2 - MgO-170 having a bulk density of about 560 g/l, particle size 2-25 $\mu$m.

3 - Detergency nonionic, being a narrow range ethoxylate Novel II 1012-61.5 ex Vista)

4 - Non-detergency nonionic being Synperonic A3 ex ICI

5 - Linear $C_{12}$ alkyl benzene sulphonic acid.

Example II

The following composition was prepared as in example I.

| Ingredient (wt parts) | |
|---|---|
| $C_{10-12}$ alcohol 6.2 EO[1)] | 23.8 |
| $C_{13-15}$ alcohol 3 EO[2)] | 19.5 |
| Glycerol triacetate | 5.0 |
| alkyl benzene sulphonic acid[3)] | 6.0 |
| silicone antifoam | 1.0 |
| sodium carbonate | 18.0 |
| calcium carbonate | 7.0 |
| sodium carboxymethyl cellulose | 1.0 |
| polymer[4)] | 1.0 |
| fluorescer | 0.1 |
| HM silica[5)] | 3.0 |
| TAED | 3.0 |
| sodium perborate mono | 10.5 |
| protease[6)] | 0.4 |
| lipase[7)] | 0.3 |
| colour | 0.4 |

Notes:

-1- Vista Novel II 1012-62 (100%) ex Vista

-2- Synperonic A3 ex ICI

-3- Marlon AS3 ex Huls

-4- Versa TL3 (100 %) ex National Starch

-5- Sipernat D17® (100%) ex Degussa

-6- Savinase 16SL® ex Novo

-7- Lipolase 100SL® ex Novo

## Claims

1. A liquid non-aqueous detergent composition comprising nonionic surfactants, characterised in that the nonionic surfactant is a mixture of:
   (a) one or more detergency nonionic materials selected from the group consisting of alkoxylated fatty alcohols, said alcohol comprising on average more than 9 and less than 12 carbon atoms and being alkoxylated with on average more than 5 and less than 10 alkoxygroups selected from ethoxy and/or propoxy groups; and
   (b) one or more nonionic non-detergency ingredients, which are selected from the groups of alkoxylated fatty alcohols, said alcohol comprising on average from 12 to 16 carbon atoms and being alkoxylated with on average less than 5 alkoxy groups selected from ethoxy and/or propoxy groups, and fatty alcohols having a carbon chain length of from 9 to 15.

2. A composition according to claim 1, wherein the detergency nonionic material additionally satisfies one or more of the following conditions:

(a) the material has an HLB value of more than 12;
(b) the material has a conductivity of more than 10 x $10^{-4}$ $ohm^{-1}$ $m^{-1}$;
(c) the material has a standard foam height of more than 40 mm.

3. A composition according to claim 1, wherein the detergency nonionic material comprises an ethoxylated alcohol having an average of from 5 to 8 ethylene oxide (EO) groups per molecule, at least 60% having a number of ethylene oxide groups within ±2EO of the average and the alkyl chain distribution being such that less than 2% has a chain length of 9 or less carbon atoms, at least 90% has a chain length between 10 and 12 carbon atoms and less than 10% has a chain length of 13 or more carbon atoms, said percentages being by weight of the ethoxylated alcohol.

4. A composition according to claim 1, wherein the nonionic non-detergency ingredient additionally satisfies one or more of the following conditions:
(a) the ingredient has an HLB value of less than 12;
(b) the ingredient provides a standard conductivity reduction of at least 10%.
(c) the ingredient provides a standard foam height reduction of at least 30%.
(d) the ingredient provides a standard viscosity reduction of at least 100 mPas at $21s^{-1}$.

5. Composition according to claim 1, wherein the nonionic non-detergency ingredient is selected from the group consisting of alkoxylated fatty alcohols comprising a C10-14 alkyl chain ethoxylated with from 2 to 4 ethoxy groups and fatty alcohols comprising from 10-14 carbon atoms or mixtures thereof.

6. Composition according to claim 1, wherein the weight ratio of the detergency nonionic material to the nonionic non-detergency ingredient is from 10 : 1 to 1 : 5.

7. A composition according to one or more of the preceding claims comprising:
(a) at least 10 % by weight of a liquid phase, at least 80 to 100 % by weight thereof being a mixture of a detergency nonionic material and a nonionic non-detergency ingredient;
(b) 10 - 90 % by weight of suspended solids;
(c) 0.1 - 15 % by weight of a deflocculant material;
(d) 5.5 - 27 % by weight of a peroxy bleach compound;
(e) 0.5 - 14 % by weight of a bleach activator.

8. Use of a nonionic non-detergency ingredient selected from the groups of alkoxylated fatty alcohols said alcohol comprising on average from 12 to 16 carbon atoms and being alkoxylated with on average less than 5 alkoxy groups selected from ethoxy and/or propoxy groups, and fatty alcohols having carbon chain length of from 9 to 15 as a foam and/or viscosity control agent in a liquid non-aqueous detergent composition.

## Patentansprüche

1. Flüssiges nichtwässeriges Waschmittel, umfassend nichtionische Tenside, dadurch gekennzeichnet, daß das nichtionische Tensid ein Gemisch ist aus:
(a) einem oder mehreren waschaktiven nichtionischen Stoffen, ausgewählt aus der Gruppe, bestehend aus alkoxylierten Fettalkoholen, wobei der Alkohol im Durchschnitt mehr als 9 und weniger als 12 Kohlenstoffatome umfaßt und alkoxyliert ist mit im Durchschnitt mehr als 5 und weniger als 10 Alkoxygruppen, ausgewählt aus Ethoxy- und/oder Propoxygruppen; und
(b) einem oder mehreren nichtionischen nichtwaschaktiven Bestandteilen, ausgewählt aus den Gruppen von alkoxylierten Fettalkoholen, wobei der Alkohol im Durchschnitt 12 bis 16 Kohlenstoffatome umfaßt und mit im Durchschnitt weniger als 5 Alkoxygruppen alkoxyliert ist, ausgewählt aus Ethoxy- und/oder Propoxygruppen, und Fettalkoholen mit einer Kohlenstoffkettenlänge von 9 bis 15.

2. Mittel nach Anspruch 1, wobei der waschaktive nichtionische Stoff zusätzlich einer oder mehrerer der nachstehenden Bedingungen genügt:
(a) der Stoff hat einen HLB-Wert von mehr als 12;
(b) der Stoff hat eine Leitfähigkeit von mehr als 10 x $10^{-4}$ $\Omega^{-1}m^{-1}$;
(c) der Stoff hat eine Standardschaumhöhe von mehr als 40 mm.

3. Mittel nach Anspruch 1, wobei der waschaktive nichtionische Stoff einen ethoxylierten Alkohol mit im Durchschnitt 5 bis 8 Ethylenoxidgruppen (EO) pro Molekül umfaßt, wobei mindestens 60 % eine Anzahl an Ethylenoxidgruppen innerhalb ±2EO des Durchschnittes aufweisen und die Alkylkettenverteilung derart ist, daß weniger als 2 % eine Kettenlänge von 9 oder weniger Kohlenstoffatomen aufweisen, mindestens 90 % eine Kettenlänge zwischen 10 und 12 Kohlenstoffatomen aufweisen und weniger als 10 % eine Kettenlänge von 13 oder mehr Kohlenstoffatomen aufweisen und wobei die Prozentangaben auf das Gewicht des ethoxylierten Alkohols bezogen sind.

4. Mittel nach Anspruch 1, wobei der nichtionische nichtwaschaktive Bestandteil zusätzlich einer oder mehrerer der nachstehenden Bedingungen genügt:
   (a) der Bestandteil hat einen HLB-Wert von weniger als 12;
   (b) der Bestandteil liefert eine Verminderung der Standardleitfähigkeit von mindestens 10 %;
   (c) der Bestandteil liefert eine Verminderung der Standardschaumhöhe von mindestens 30 %;
   (d) der Bestandteil liefert eine Verminderung der Standardviskosität von mindestens 100 mPas bei 21 $s^{-1}$.

5. Mittel nach Anspruch 1, wobei der nichtionische nichtwaschaktive Bestandteil ausgewählt ist aus der Gruppe, bestehend aus alkoxylierten Fettalkoholen, umfassend eine C10-14-Alkylkette, die mit 2 bis 4 Ethoxygruppen und Fettalkoholen ethoxyliert ist, umfassend 10-14 Kohlenstoffatome, oder Gemischen davon.

6. Mittel nach Anspruch 1, wobei das Gewichtsverhältnis des waschaktiven nichtionischen Stoffes zu dem nichtionischen nichtwaschaktiven Bestandteil 10:1 bis 1:5 beträgt.

7. Mittel nach einem oder mehreren der vorangehenden Ansprüche umfassend:
   (a) mindestens 10 Gew.-% einer Flüssigphase, wobei mindestens 80 bis 100 Gew.-% davon als Gemisch eines detergenzaktiven nichtionischen Stoffes und eines nichtionischen nichtwaschaktiven Bestandteils vorliegen;
   (b) 10 - 90 Gew.-% suspendierte Feststoffe;
   (c) 0,1 - 15 Gew.-% eines Entflockungsstoffes;
   (d) 5,5 - 27 Gew.-% einer Peroxybleichmittelverbin dung;
   (e) 0,5 - 14 Gew.-% eines Bleichmittelaktivators.

8. Verwendung eines nichtionischen nichtwaschaktiven Bestandteils, ausgewählt aus der Gruppe alkoxylierter Fettalkohole, wobei der Alkohol im Durchschnitt 12 bis 16 Kohlenstoffatome umfaßt und mit im Durchschnitt weniger als 5 Alkoxygruppen, ausgewählt aus Ethoxy- und/oder Propoxygruppen, alkoxyliert ist und Fettalkoholen mit Kohlenstoffkettenlängen von 9 bis 15 als Schaum- und/oder Viskositätsregelungsmittel in einer flüssigen nichtwässerigen Waschmittelzusammensetzung.

## Revendications

1. Une composition détergente liquide non aqueuse contenant des agents tensioactifs non ioniques, caractérisée en ce que l'agent tensioactif non ionique est un mélange de :
   (a) un ou plusieurs matériaux non ioniques détergents sélectionnés parmi le groupe comprenant des alcools gras alkoxylés, ledit alcool contenant en moyenne plus de 9 et de moins de 12 atomes de carbone, et étant alkoxylé avec en moyenne plus de 5 et moins de 10 groupes alkoxy, sélectionnés parmi des groupes éthoxy et/ou propoxy ; et
   (b) un ou plusieurs ingrédients non détergents non ioniques, qui sont sélectionnés parmi les groupes d'alcools gras alkoxylés, ledit alcool contenant en moyenne 12 à 16 atomes de carbone et étant alkoxylé avec en moyenne moins de 5 groupes alkoxy sélectionnés parmi des groupes éthoxy et/ou propoxy et des alcools gras ayant une longueur de chaîne de carbone allant de 9 à 15.

2. Une composition selon la Revendication 1, dans laquelle le matériau non ionique détergent satisfait en outre à une ou plusieurs des conditions suivantes :
   (a) le matériau a une valeur HLB de plus de 12 ;
   (b) le matériau présente une conductivité de plus de 10 x $10^{-4}$ $ohm^{-1}$ $m^{-1}$ ;
   (c) le matériau génère une mousse de hauteur standard supérieure à 40 mm.

3. Une composition selon la Revendication 1, dans laquelle le matériau non ionique détergent contient un alcool éthoxylaté ayant une moyenne de 5 à 8 groupes d'oxydes d'éthylène (EO) par molécule, au moins 60 % ayant un nombre de groupes d'oxyde d'éthylène à l'intérieur de +/- 2EO de la moyenne et la distribution de chaîne alkyle étant telle que moins 2 % ont une longueur de chaîne de 9 atomes de carbone, ou moins, au moins 90 % ont une longueur de chaîne située entre 10 et 12 atomes de carbone, et moins de 10 % ont une longueur de chaîne de 13 atomes de carbone ou plus, lesdits pourcentages étant des pourcentages en masse de l'alcool éthoxylaté.

4. Une composition selon la Revendication 1, dans laquelle le matériau non ionique non détergent satisfait en outre à une ou plusieurs des conditions suivantes :
   (a) l'ingrédient a une valeur HLB de moins de 12 ;
   (b) l'ingrédient fournit une réduction de conductivité standard d'au moins 10 % ;
   (c) l'ingrédient génère une réduction de hauteur de mousse standard d'au moins 30 % ;
   (d) l'ingrédient fournit une réduction de viscosité standard d'au moins 100 mPa.s à $21^{s-1}$.

5. Une composition selon la Revendication 1, dans laquelle le matériau non ionique non détergent est sélectionné parmi le groupe composé d'alcools gras alkoxylés contenant une chaîne alkyle en $C_{10}$-$C_{14}$ éthoxylatée avec 2 à 4 groupes éthoxy et des alcools gras contenant de 10 à 14 atomes de carbone ou des mélanges de ceux-ci.

6. Une composition selon la Revendication 1, dans laquelle le rapport en masse du matériau non ionique détergent à l'ingrédient non détergent non ionique va de 10:1 à 1:5.

7. Une composition selon une ou plusieurs des Revendications précédentes contenant :
   (a) au moins 10 % en masse d'une phase liquide, de préférence 80 à 100 % en masse de celle-ci étant un mélange d'un matériau non ionique détergent et d'un ingrédient non détergent non ionique ;
   (b) 10 à 90 % en masse de solides en suspension ;
   (c) 0,1 à 15 % en masse d'un matériau défloculant ;
   (d) 5,5 à 27 % en masse d'un composé de blanchiment peroxy ;
   (e) de 0,5 à 14 % en masse d'un activateur de blanchiment.

8. Utilisation d'un ingrédient non détergent non ionique sélectionné parmi les groupes d'alcools gras alkoxylés, ledit alcool contenant en moyenne 12 à 16 atomes de carbone et étant alkoxylé avec en moyenne moins de S groupes alkoxy sélectionnés parmi des groupes éthoxy et/ou propoxy et des alcools gras ayant une longueur de chaîne de carbone allant de 9 à 15, en tant qu'agent de contrôle de mousse et/ou de viscosité dans une composition détergente liquide non aqueuse.