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(54) Title: LIQUID CLEANING PRODUCTS

(57) Abstract

A substantially non-aqueous liquid cleaning product composition comprises a substantially non-aqueous liquid phase and also comprises a certain kind of polymer. The total composition is shear-thinning (viscosity decreases with shear rate). The equivalent composition without the solids is also shear-thinning but to a lesser or equal extent.
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LIQUID CLEANING PRODUCTS

Technical field
The present invention relates to substantially non-aqueous liquid cleaning products which comprise a non-aqueous liquid phase, optionally with a dispersed particulate solid material. Non-aqueous liquids are those containing little or no water. The non-aqueous liquid phase may comprise a liquid surfactant and/or a liquid non-surfactant suitable for use in a cleaning product.

Background & prior art
Most commonly, particulate solids are those which have beneficial auxiliary effects in use, for example for fabrics washing, they may comprise detergency builders to counteract water hardness, as well as bleaches. For hard surface cleaning applications, the solids could comprise abrasive particles.

It is also often desired to add one or more ingredients to these systems in order to provide one or more of the following advantages:

(a) to improve the solid suspending properties of the system;
(b) to reduce the clear layer formation upon storage;
(c) to reduce the need of other stabilising materials;
(d) to reduce ashing in fabric washing applications;
(e) to reduce the consistency of the product;
(f) to provide an increased tolerance for high levels of solid materials in the system; and
(g) to reduce the setting of the system upon storage.

We have now found that improved benefits such as of one or more of the types (a) to (g) recited hereinbefore may be obtained in non-aqueous liquid detergent compositions comprising a specific kind of polymer material.
EP 413 616 discloses non-aqueous liquids comprising carboxy-containing polymers to provide stability and improved water dispersibility.

EP 359 491 and EP 359 492 disclose non-aqueous liquids comprising respectively low and high molecular weight vinylpyrrolidone polymers.

EP 28 849 discloses non-aqueous liquids comprising a stabilising polymer that is an at least partially hydrolyzed copolymers of maleic anhydride with ethylene or vinylmethylether.

GB 2,228,944 discloses non-aqueous liquids comprising polymeric materials that may comprise acrylamide monomers.

Non-pre-published EP 510 762 discloses non-aqueous liquids comprising polymers that may comprise 2-acrylamide-2 methyl propane sulphonic acid as monomer B.

Description of the invention
Polymers according to the invention have the property that when added to the non-aqueous liquid phase in the absence of the solids, the viscosity of the liquid phase reduces with shear rate and when added to the same liquid phase in the presence of the solid material, still causes a contribution to viscosity reduction for a given change in shear rate which, at least over the shear thinning region (typically less than 400 s⁻¹), is greater than for the liquid phase in the presence of the solids or polymer alone.

Thus according to one aspect of the invention there is provided a substantially non-aqueous liquid cleaning product composition comprising a substantially non-aqueous liquid phase, the composition further comprising a polymer which
(a) when added to the substantially non-aqueous liquid phase in the absence of the solid material causes the viscosity of said liquid phase to reduce with shear rate; and

(b) when added to the substantially non-aqueous liquid phase in the presence of the solid material causes the viscosity of the liquid phase to reduce with shear rate but such that the gradient of the viscosity versus shear rate curve is greater than or equal to that in case (a).

Rheological properties
In principle, any solid may be suspended without sedimentation in a non-aqueous liquid phase if a strong enough structure is created in the liquid phase. By way of analogy, it may be appreciated aqueous liquids can be made to suspend particulate solids, either by addition of a cross-linking thickening polymer, eg. of the "Carbopol" (Trade Mark) type, or else by creating an appropriate liquid crystalline phase using the functional ingredients of the composition themselves.

However, for the composition (whether aqueous or non-aqueous) to be pourable, the structure must at least partially break-down or be modified under shear. In other words the viscosity must reduce with increased shear rate. In some aqueous systems where the structure consists of multi-bilayer vesicles of surfactant molecules, it is only necessary for the vesicles to deform and "roll-over" each other to achieve this effect.

We have found that in non-aqueous systems, the required shear thinning behaviour can be obtained by incorporation of the specific polymer materials referred to above.

Without wishing to be bound by any theory or interpretation, the applicants have conjectured that
suitable polymer materials are self-associative thickeners. That is to say, when incorporated in the composition in an appropriate amount they increase its viscosity, without appreciable absorption onto the solid particles. Thus it is interactions between the polymer molecules themselves which gave rise to the desired properties. Such interactions could, for example, be strong due to cross-linking through co-valent bonding or be the result of weaker forces such as hydrogen bonding or van der Waal's interactions.

Cross-linking could be the direct result of reaction of functional groups present on pendant side-chains of the polymer molecules and/or the result of incorporation of specific cross-linking agents added for the purpose. Whilst such cross-linking agents usually will have lower molecular weights than the molecular weights of the polymer(s), they can still be relatively high (eg. >1000).

Since the essence of the present invention is the discovery of a general principle and not just certain combinations of defined ingredients, the applicants do not wish the scope of protection defined by the appended claims to be limited to the combinations exemplified herein, either generically or specifically. For that reason, the present invention is hereinbefore defined, and also in the claims, in terms of polymers selected to endow certain properties to the liquid phase with and without the solid ingredients.

However, the aforementioned requirement is primarily directed to selection of ingredients in advance, prior to formulation for the first time, of a specific new composition in accordance with the present invention. It is also desirable to have a test which will identify whether a composition once prepared is in accordance with the present invention. The following is a non-limiting example of such a test. That is to say, if a non-aqueous solid-containing composition yields a positive result in such a test, it is
a composition according to the present invention, although it is possible that a few compositions according to the present invention, particularly those with high volume fractions of solids (eg. >0.3), may give an equivocal or negative result in this test.

The principle of the test is that most non-aqueous dispersions of particulate solids contain a relatively high volume fraction of solids. In any sedimentation resulting in formation of a clear layer, the smaller solid particles will be taken down with sedimentation of the larger particles. Any polymer structures in the liquid phase, even if dissolved, will also have a tendency to sediment with the solids.

Thus according to the test, a given composition should be diluted with the same, or substantially the same component(s) of its liquid phase and either allowed to sediment over a period of time or else centrifuged gently. If the viscosity of the remnant clear layer decreases (typically more than 10 mPas) with increased shear rate (eg. somewhere in the range 0.01 to 200s⁻¹), and contains at least some of the polymer, then the polymer is a polymer as specified as a component of compositions according to the present invention.

The polymer
Preferred polymers for use as the polymer ingredient of compositions according to the present invention are block co-polymers, that may be randomly ordered, containing at least one group soluble in the non-aqueous liquid phase which group is also capable of self-association with a like group of another polymer molecule when the polymer is dissolved in said liquid phase. Examples of such soluble self-associating groups are amine, amide and C₁₀₋₂₂ alkyl groups. Of these, amines and amides are especially preferred.
The polymers also contain at least one other group soluble in the non-aqueous liquid phase, which other group links two or more of the self-associating groups together and is substantially non-absorbent on the solid particles. Typical other groups are homopolymers such as polyethylene oxide, polyvinyl pyrrolidone and co-polymers made from commercially available vinyl monomers such as acrylic acid, maleic acid, vinyl pyrrolidone, vinyl alkyl ethoxylates, vinyl alcohol, vinyl alky, lates and vinyl ethoxy alkylates.

Generally speaking, the mutually associating group(s) will constitute from 0.001% to 20% of the average polymer molecular weight, preferably from 0.01% to 10% and most preferably from 0.02 to 5%.

The polymer as a whole will usually be used at 0.1% to 10%, preferably from 0.1% to 5% and most preferably from 0.5% to 2% by weight of the total composition according to the present invention.

Thus, preferred polymers include those polymer that comprise:

(i) 2 groups A, which exhibits self association when the polymer is dissolved in a non-aqueous liquid medium having a dielectric constant from 1 to 20;
(ii) from 10 to 1000 groups B which is a monomeric or polymeric group soluble in the non-aqueous liquid phase; and
(iii) 0 or from 1 to 15 of groups B-A.

More preferred polymers include those of formula (I)

\[ A-(B)_x-(B-A)_y-A \] (I)
where

x is from 10 to 1000;

y is 0 or else y is from 1 to 15;

A is a group which exhibits self-association when the polymer is dissolved in a non-aqueous liquid medium having a dielectric constant of from 1 to 20; and

B is any monomeric or polymeric group soluble in the non-aqueous liquid phase.

Most preferably, y is less than 8, especially from 0 to 3. Preferably, x is from 20 to 200.

Preferred entities for group A include $-\text{NH}_2$, $-\text{CONR}^1\text{R}^2$, wherein $\text{R}^1$ and $\text{R}^2$ are independently selected from hydrogen and alkyl groups have less than 20 carbon atoms, $\text{C}_{10-22}$ alkyl groups (preferably $\text{C}_{10-18}$) and mixtures thereof. More preferred entities for group A are $-\text{NH}_2$ and $-\text{CONR}^1\text{R}^2$.

Preferably, $\text{R}^1$ and $\text{R}^2$ are independently selected from hydrogen and $\text{C}_1-\text{C}_{10}$ alkyl, and more preferably from hydrogen and $\text{C}_1-\text{C}_6$ alkyl. Preferably, $\text{R}^1+\text{R}^2$ in total contain less than 12 carbon atoms.

Preferred entities for group B include $-(\text{CH}_2-\text{CH}_2\text{O})_n-$, especially when $n$ is from 20 to 200, vinylpyrrolidone, polyvinylpyrrolidone (i.e. [vinylpyrrolidone]$_n$, wherein $n$ is from 15 to 300), vinyl acetate, vinyl alcohol, acrylic acid, methacrylic acid, and half esters of maleic anhydride especially when co-polymerised with acrylic acid in a mole ratio of from 1:1 to 0.2:1.

The average molecular weight of the polymer material as determined by aqueous gel permeation chromatography using polyacrylate standards is preferably from 1000 to 100,000,
more preferably from 2000 to 80,000, and most preferably from 5000 to 50,000. The determination method is based on aqueous phosphate buffer eluant using Toya Soda and Polymer Laboratories aqueous GPC columns with an ultraviolet detector set at 215 nm. For polymers having no chromophore at 215 nm, a refractive index detector may be used.

It is preferred for the polymer to be prepared in-situ in one or more or all of the component(s) of the non-aqueous liquid phase to be used as the non-aqueous liquid phase. This can be achieved using methods known in the art, for example as described in F. Billmeyer, Textbook of Polymer Science, Wiley Interscience.

In the alternative, the polymer may be prepared in isolation and subsequently pre-dissolved in the non-aqueous liquid phase before the solids are added.

Post dosing of separately prepared polymer, after incorporation of some or all of the solids in the non-aqueous liquid phase is also possible, especially if the composition also contains a deflocculating agent (vide infra).

Product form
All compositions according to the present invention are liquid cleaning products. In the context of this specification, all references to liquid cleaning products refer to those product 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. Preferably compositions of the
invention are formulated as agents for washing and/or conditioning of fabrics.

Thus, the compositions will contain at least one agent which promotes the cleaning and/or conditioning of the article(s) in question, selected according to the intended application. Usually, this agent will be selected from surfactants, enzymes, bleaches, builders, buffers, 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.

If compositions of the invention are fabric cleaning products they preferably contain a liquid phase containing nonionic surfactants and a solid phase dispersed in the liquid phase, said solid phase comprising one or more of the following ingredients bleaches, bleach activators, builders and solid surfactants.

If compositions of the invention are intended for other uses, for example for mechanical warewashing, sometimes the liquid phase will comprise a solvent material other than nonionic surfactant such as for example glyceroltriacetate, paraffin, a low molecular weight polyethylene glycol or an ethoxylated polyethylene glycol. The solid phase of the product will then generally comprise one or more of builders, abrasive materials and solid surfactant materials.

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.

Non-ionic surfactants
Nonionic detergent surfactants are well-known in the art. They normally consist of a water-solubilizing polyalkoxyylene or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived, for example, from alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 12 carbon atoms, primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes.

Also common are fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkylolyl group having from 1 to 3 carbon atoms. In any of the mono- and di- alkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule.

In all polyalkoxyylene containing surfactants, the polyalkoxyylene moiety preferably consists of an average of from 2 to 20 groups of ethylene oxide or of ethylene oxide and propylene oxide groups. Amongst the latter class,
particularly preferred are those described in the applicants' published European specification EP-A-225,654, especially for use as all or part of the liquid phase. Also preferred are those ethoxylated nonionics which are the condensation products of fatty alcohols with from 9 to 15 carbon atoms condensed with from 3 to 11 moles of ethylene oxide. Examples of these are the condensation products of C11-13 alcohols with (say) 3 to 7 moles of ethylene oxide. These may be used as the sole nonionic surfactants or in combination with those of the described in the last-mentioned European specification, especially as all or part of the liquid phase.


Mixtures of different nonionic detergent surfactants may also be used. Especially preferred is the combined use of detergency nonionics with non-detergency nonionics, for example mixtures of alkoxylated fatty alcohols containing 5-10 EO groups and alkoxylated alcohols containing 2-4 EO groups.

Mixtures of nonionic detergent surfactants with other detergent surfactants such as anionic, cationic or amphotolytic detergent surfactants and soaps may also be used.

Preferably the level of nonionic surfactants in the composition is from 1 to 90 % by weight, more preferably 5 to 75 %, most preferably 20 to 60 %.

Anionic surfactants
Examples of suitable anionic detergent surfactants are
alkali metal, ammonium or alkylolamine salts of alkylbenzene sulphonates or primary alkyl sulphates having from 10 to 18 carbon atoms in the alkyl group, alkyl and alkylether sulphonates having from 10 to 24 carbon atoms in the alkyl group, the alkylether sulphonates having from 1 to 5 ethylene oxide groups, and olefin sulphonates prepared by sulphonation of C10-24 alpha-olefins and subsequent neutralization and hydrolysis of the sulphonation reaction product and all stable free acid forms of such anionic surfactants.

The non-aqueous liquid phase
As a general rule, the most suitable liquids to choose as the liquid phase are those organic materials having polar molecules. In particular, those comprising a relatively lipophilic part and a relatively hydrophilic part, especially a hydrophilic part rich in electron lone pairs, tend to be well suited. This is completely in accordance with the observation that liquid surfactants, especially polyalkoxyolated nonionics, are one preferred class of material for the liquid phase.

Non-surfactants which are suitable for use as the liquid phase include those having the preferred molecular forms referred to above although other kinds may be used, especially if combined with those of the former, more preferred types. In general, the non-surfactant solvents can be used alone or with in combination with liquid surfactants. Non-surfactant solvents which have molecular structures which fall into the former, more preferred category include ethers, polyethers, alkylamines and fatty amines, (especially di- and tri-alkyl- and/or fatty-N-substituted amines), alkyl (or fatty) amides and mono- and di-N-alkyl substituted derivatives thereof, alkyl (or fatty) carboxylic acid lower alkyl esters, ketones, aldehydes, and glycerides. Specific examples include respectively, di-alkyl ethers, polyethylene glycols, alkyl
ketones (such as acetone) and glyceryl trialkylcarboxylates (such as glyceryl tri-acetate, hereinafter referred to as GTA), glycerol, propylene glycol, and sorbitol.

Many light solvents with little or no hydrophilic character are in most systems, to a small extent, unsuitable on their own. Examples of these are lower alcohols, such as ethanol, or higher alcohols, such as dodecanol, as well as alkanes and olefins. However, they can be combined with other liquid materials.

Proportion of liquid 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 60% by weight of the composition.

Solids content
Compositions of the invention may comprise a solid phase dispersed in the liquid phase. 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.

If present, in general, the solids content of the product may be within a very wide range, e.g. higher than 5%, for example from 10-90%, usually from 30-80% and preferably from 40-65% by weight of the final composition.

The solid phase should be in particulate form and have a D(3,2) 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. For the purpose of the present invention references to average particle diameter refer to the D(3,2) particle size, which is a surface, volume mean diameter calculated as described by M. Alderliesten, Anal. Proc. Vol. 21, May, 1984, 167-172. Hereinafter, any reference to average or mean particle size or diameter refers to the D(3,2) average unless explicitly stated to the contrary.

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
Surprisingly, it has been found that the physical stability of non-aqueous liquid detergent compositions can be even further improved and/or setting problems can be minimised, if hydrophobically modified dispersants (hereinafter termed HM materials) are used.
For the purpose of the present invention, a dispersant material is a material, of which the main purpose is to stabilize 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 micrometers, more preferred 0.01 to 3 micrometers, most preferred from 0.02 to 0.5 micrometer. The amount 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 hydrophobic modification treatment. Suitable reactions include esterification or etherification of the hydrophilic groups. Preferably the hydrophobic modification 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 hydrophobic modification.

Preferably HM silica containing dispersants are used. The hydrophobic modification 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 or silyl group. More preferably the surface hydroxy-groups are substituted by methyl groups.

For even greater reduction the clear layer separation of liquid detergent compositions of the invention, it has been found that the use of 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 micrometers, more preferably from 0.5 to 100 micrometers, most preferably from 2 to 70 micrometers. The level of metal oxide is preferably from 0.1 to 7 % by weight of the composition, more preferably from 0.5 to 5 %, most preferably 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 triopolyphosphates, 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 polyhydroxysulphonates. 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. Preferably the level of builder materials is from 0-60%, more preferred 5-50, most preferred 10-40% by weight.

Deflocculants
Preferably compositions of the invention also comprise one or more deflocculant materials. In principle, any material may be used as a deflocculant provided it fulfils the deflocculation test described in European Patent Specification EP-A-266 199 (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.

Deflocculants are preferably selected from Bronsted acids and Lewis acids. Examples thereof are transition metals, anhydrides, organic acids, inorganic mineral acids and salts, $C_8$-$C_{20}$ fatty acids and salts, $C_1$-$C_{10}$ alkanoic acids, substituted anhydrous alkali-metal aluminosilicate, alkyl, alkenyl aryl, aralkyl and aralkenyl sulphonlic or carboxylic acids and salts and halogenated derivatives thereof, zwitterionic surfactants and anionic surfactants of the formula R-L-A-Y as defined in EP 266199. The acid form is preferably used.

Some typical examples of deflocculants include the alkanoic acids such as acetic, propionic and stearic acids and their halogenated counterparts such as trichloracetic and trifluoracetic as well as the alkyl (e.g. methane) sulphonic acids and aralkyl (e.g. paratoluene) sulphonlic 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, tetrachlorometano 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 of such surfactants. 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 C10-C22 fatty acids and dimers thereof, the C8-C18 alkylbenzene sulphonic acids, the C10-C18 alkyl- or alkylether sulphuric acid monoesters, the C12-C18 paraffin sulphonic acids, the fatty acid sulphonic acids, the benzene-, toluene-, xylene- and cumene sulphonic acids and so on. Particularly preferred are the linear C12-C18 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-266 199, 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. Surprisingly, however it has been found that for obtaining stability, in compositions of the invention generally the presence of the polymer material reduces the need for high levels of deflocculant material.

Bleach

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 peroxo 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 7% by weight.

Typical examples of the suitable peroxybleach compounds are alcalimetal 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 1% by weight, preferably between about 0.1% and about 0.5% 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. However, solid bleach precursors such as N, N, N, N\(^1\), N\(^1\) -tetraacetyl ethylene diamine (TAED) may also be used.

**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 deperfumes), 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, amylyolytic enzymes and lipolytic enzymes (lipases). Various types of proteolytic enzymes and amylyolytic enzymes are known in the art and are commercially available. They may be incorporated as "prills", "marumes" or suspensions.

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 cellulosics, e.g. sodium carboxymethyl cellulose (SCMC), anionic poly-electrolytes, especially polymeric aliphatic carboxylates, or organic phosphonates.
Water

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.

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

The appropriate stage for incorporating the polymer has been discussed hereinbefore. The following is a description of preferred ways of bringing together and processing the solids and the non-aqueous liquid phase.

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.

However, compositions which have a Bingham yield stress of 5 Pa. or more may be formulated with large particulate solids, for example speckles or balls included for endowing the composition with aesthetic appeal, or large functional solids such as abrasives if it is desired to formulate a liquid abrasive cleaner. The aforementioned value of 5 Pa. as Bingham yield stress refers to that determined in the shear rate range of from 0.1 to 400 s\(^{-1}\) at 25\(^\circ\)C after equilibration for one minute.

A preferred combination of such mills for achieving a particle size of 0.1 to 100 microns 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**

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<td>Synperonic A3 (2)</td>
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<td>Glycerol triacetate</td>
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<td>Silicone oil anti-foam (DB100)</td>
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<tr>
<td>Sipernat D17 (6)</td>
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<td>Sodium Perborate</td>
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<tr>
<td>SCMC</td>
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<td>Tinopal CBS-X, fluorescer</td>
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<tr>
<td>Perfume</td>
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<tr>
<td>Polymer</td>
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</table>

**Example 1 - Result**

Clear upper layer

25 after one months

Polymer Viscosity mPa.s at 21s⁻¹ storage at 37°C

30 No polymer 980 7mm

Rheovis CRX (dry solid)
ex Allied Colloids 1120 4mm

35 A=NH₂, B=ethylene oxide
Ratio 2:1, Mw=4000 1300 2.5mm
A=NH₂, B=ethylene oxide
Ratio 2:1, Mw=8000
1280  3mm

A=NH₂, B=ethylene oxide
5 Ratio 2:1, Mw = 1500
1104  3mm

A-B-A₁-B-A polymer
A=NH₂, B=ethylene oxide
Mw = 8000, A₁ =
10 CO₂CH₂CH₂NHCH₂CH₂CO₂⁻  1420  1mm

Poly (Acrylic acid co acrylamide)
random copolymer Monomer ratio
5:1, Mw 10,000
1240  2mm

Poly (Acrylic Acid co Acrylamide)
random copolymer Monomer ratio
5:1, Mw 20,000
1510  1mm

Hydrolysed Poly(Vinyl) acetate
co-acrylamide) Monomer ratio 10:1,
Mw 15,000
1200  3.5mm

Comparative examples:

Polyacrylic acid
Mw 20,000 (GB 2,228,944)
1010  7.5mm

Poly vinylalcohol Mw 10,000
1080  6.5mm

Poly vinyl pyrrolidone
Mw 40,000 (EP 359492)
1103  6.5mm

Gantrez AN-119, dodecanol half
ester (EP 413 616)
1130  6mm
EXAMPLE 2

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<td>Anti-foam (8)</td>
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<td>TAED</td>
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<td>Sodium Perborate</td>
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<td>Sodium Stearate</td>
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<td>Perfume</td>
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<tr>
<td>Polymer</td>
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Results

Time to form 1cm of clear upper layer at 37°C of a 1 litre sample in a 10cm diameter container

20 No polymer                     2 days

Rheovis CRX (dry solid) ex Allied Colloids 6 days

30 A=NH₂, B=ethylene oxide
   Ratio 2:1, Mw = 4000 10 days

A = NH₂, B=ethylene oxide
   Ratio 2:1, Mw = 8000 8 days

35 A = -NH₂ B=ethylene oxide
   Ratio 2:1, Mw = 15000 16 days
A-B-Al-B-A polymer
A = -NH₂, B=ethylene oxide
Mw = 8000, Al= CO₂CH₂CH₂NHCH₂CH₂CO₂-

5 Poly (Acrylic acid co acrylamide) random
copolymer Monomer ratio 5:1, Mw 10,000 20 days

Poly (Acrylic acid co acrylamide) random
copolymer Monomer ratio 5:1, Mw 20,000 40 days

10 Raw Materials
(1) Narrow range ethoxylated nonionic ex Vista
(2) Cl₃-15 alcohol alkoxylated with on average 3 EO groups
ex ICI
(3) Anionic detergent in acid form ex Huls
(4) High surface area calcium carbonate
(5) Copolymer of sulphonated styrene and maleic anhydride,
Na salt, ex National Starch & Chemical Co.
(6) Hydrophobically modified silica dispersant ex
Degussa
(7) Marlipal 013 materials are ethoxylated
isotridecanol. 013/30 contains 30% ethylene oxide
and 013/60 60% ethylene oxide Ex Hoechst
(8) DB100® ex Dow Corning

25
30

CLAIMS

1. A substantially non-aqueous liquid cleaning product composition comprising a substantially non-aqueous liquid phase, the composition further comprising a polymer of formula (I)

\[ A-(B)_x-(B-A)_y-A \]  \hspace{1cm} (I)

wherein:

\( x \) is from 10 to 1000;

\( y \) is from 0 to 15;

\( A \) is a group which exhibits self association when the polymer is dissolved in a non-aqueous liquid medium having a dielectric constant from 1 to 20;

\( A \) constitutes from 0.001% to 20% of the average polymer molecular weight and comprises entities selected from \(-\text{NH}_2\), \(-\text{CONR}^1\text{R}^2\), wherein \( \text{R}^1 \) and \( \text{R}^2 \) are independently selected from hydrogen and alkyl groups having less than 10 carbon atoms, a \( \text{C}_{10-22} \) alkyl group and mixtures thereof; and

\( B \) is a monomeric or polymeric group soluble in the non-aqueous liquid phase.

2. A composition according to claim 1, wherein the group \( B \) is a polyethoxy, vinylpyrrolidone, polyvinylpyrrolidone, vinyl acetate, vinyl alcohol, acrylic acid, methacrylic acid half-ester of maleic anhydride or a half-ester of maleic anhydride copolymerised with acrylic acid in a mole ratio of from 1:1 to 0.2:1 group.
3. A composition according to claims 1-2, wherein the average molecular weight of the polymer is from 1000 to 100,000.

4. A composition according to claims 1-3, wherein the amount of the polymer is from 0.1 to 10% by weight of the total composition.

5. A composition according to claims 1-4, wherein a particulate solid material is dispersed in the non-aqueous phase.
INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C11D17/00

II. FIELDS SEARCHED

Minimum Documentation Searched

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Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

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- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
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- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

20 OCTOBER 1993

Date of Mailing of this International Search Report

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

SIATOU E.
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