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EUROPEAN PATENT APPLICATION

21 Application number: **84305319.0**

51 Int. Cl.⁴: **C 11 D 7/50**
C 11 D 17/00

22 Date of filing: **06.08.84**

30 Priority: **07.04.84 GB 8409054**

43 Date of publication of application:
13.11.85 Bulletin 85/46

84 Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

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84 Designated Contracting States:
CH GB LI SE AT

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84 Designated Contracting States:
BE DE FR IT LU NL

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54 **Stabilized oil-in-water cleaning microemulsions.**

57 Solvent-containing liquid detergent compositions containing degreasing solvents such as n-octyl benzene, terpenes or olefins are prepared with high levels of fatty acid/soap at a pH of ca. 6.5. The compositions are pH-adjusted to neutrality or the alkaline pH range using various amines, amine oxides or quaternary ammonium salts.

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STABILIZED OIL-IN-WATER CLEANING MICROEMULSIONS

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TECHNICAL FIELD

The present invention relates to methods for adjusting the pH of carboxylic acid-containing oil-in-water microemulsions towards the alkaline range using a variety of nitrogen-functional ingredients such as amines, quaternary ammonium salts and amine oxides. Liquid laundry detergent compositions, liquid hard surface cleaners, and the like, are thereby provided.

BACKGROUND

Various organic solvents, for example terpenes and terpene-like compounds, are rather well-known for use in hard surface cleaners for their grease removal ability. Such cleaners often contain 10 %, or more, of a solvent such as d-limonene, together with a surfactant, especially nonionic surfactants which are also well-known for their grease removal performance. Such compositions have also been suggested for cleaning carpets. British Patent 1 603 047, 1981. EPO application 81200540.3 discloses hard surface cleaners comprising a mixture of benzyl alcohol, terpenes, surfactants and other deterative ingredients.

European Patent Application 0 072 488 (August 3, 1982) suggests that terpenes such as d-limonene can be incorporated into fabric pre-treating compositions as a non-homogeneous emulsion. Such emulsions are apparently designed to be packaged in relatively small volume containers which can be shaken immediately prior to use to restore some semblance of homogeneity, then dispensed directly onto fabrics by spraying.

Clear emulsions comprising water, surfactant and various other solvents are disclosed by Davidsohn in 3rd International Congress of Surface Activity, Cologne (1960).

Terpineols, e.g. from pine oil, have been disclosed for use in wet-scouring of textiles. In particular, in 1937, U.S. Patent 2.073.464 disclosed clear compositions which can be prepared from pine oil terpineol such as alpha terpineol and fatty acid soap or free acid neutralized in situ to alkaline pH.

More recently, an article in Soap Perfumery Cosmetics April, 1983, pages 174, 175 suggests that only low levels of terpenes (3%) can be incorporated into heavy duty liquid detergents.

Citrus juices, which contain relatively low amounts of terpenes, have been suggested for use in hand soaps and dishwashing liquids. U.S. Patent 3.650.968; Mémoire descriptif 873.051 (relating to Brevet Anglais 53472/77, 22 December 1977).

The use of relatively high concentrations of solvents in heavy duty liquid laundry detergents offers many advantages. The liquid form of such products allows them to be used as pre-treatment agents. When used through-the-wash, solvents such as terpenes, certain alkyl-aromatics and certain olefin hydrocarbon solvents, have now been found to provide additional cleaning benefits over and above those provided by detergent

surfactants. Unfortunately, the non-homogeneity of compositions such as those disclosed in EPO 0 072 488 makes them inconvenient for use as a general purpose laundry detergent, since most heavy duty liquid detergents are packaged in relatively large containers which are unhandy for the user to shake thoroughly.

The present invention provides fully-formulated heavy duty liquid detergent compositions comprising as much as 20%, and higher, by weight of essentially water-insoluble solvent, in the form of homogeneous, fatty acid-built liquids that are quite suitable for use in both the fabric pre-treatment and through-the-wash laundry modes, as hard-surface cleaners, and the like.

Importantly, means are disclosed which allows such compositions to be formulated as stable microemulsions at pH's above their "as is" formulation pH of about 6.5

SUMMARY OF THE INVENTION

The present invention encompasses means for adjusting the pH of an oil-in-water microemulsion typically comprising a mixture of water (10% to 70%), grease-removal solvent or solvent mixture (5% to 20%), fatty acid or fatty acid/soap mixture (5% to 35%) and detergent surfactant (1% to 40%), together with optional detergent ingredients (generally 0.1% to 15%), by admixing therewith a nitrogen-functional material such as an amine, a quaternary ammonium salt, or an amine oxide, whereby the "as is" pH of said microemulsion is adjusted from its original pH of around 6.5 towards a neutral or alkaline pH, whereby the cleaning performance, especially enzyme cleaning action, of said microemulsion is improved.

The invention also encompasses compositions prepared in the foregoing manner, as well as methods of cleaning fabrics and hard surfaces using said compositions.

DETAILED DESCRIPTION OF THE INVENTION

The essential solvent, fatty acid (or soap) and water emulsification system, the deterative surfactant components, the means for stabilizing the formulation at pH's above 6.5, and various other optional ingredients used in the practice of the present invention are described in more detail, hereinafter. All percentages and ratios mentioned in this application are by weight, unless otherwise stated.

Solvent - The solvents employed herein can be any of the well-known "degreasing" solvents commonly known for use, in, for example, the commercial laundry and dry-cleaning industry, in the hard-surface cleaner industry and the metalworking industry. Typically, such solvents comprise hydrocarbon or halogenated hydrocarbon moieties of the alkyl or cyclo-alkyl type, and have a boiling point well above room temperature.

The formulator of compositions of the present type will be guided in the selection of solvent partly by the need to provide good grease-cutting properties, and partly by aesthetic considerations. For example, kerosene hydrocarbons function quite well in the present compositions, but can be malodorous. Kerosene can be used in commercial laundries. For home use, where malodors would not be tolerated, the formulator would be more likely to select solvents which have a relatively pleasant odor, or odors which can be reasonably modified by perfuming. Such solvents include, for example, the terpenes and terpenoid solvents obtainable from citrus fruits, especially orange terpenes and d-limonene. Benzyl alcohol is another relatively pleasant smelling solvent for use herein. Mixtures of orange terpene and benzyl alcohol are especially suitable for removing certain types of stains, e.g. marker ink, shoe polish, and dirty motor oil.

Accordingly, one preferred class of solvents used herein are the liquid paraffins, especially the "iso" C₁₀ paraffins and the mono- and bicyclic mono-terpenes, i.e., those of the hydrocarbon class, which include, for example, the terpinenes, limonenes and pinenes, and mixture thereof. Highly preferred materials of this latter type are d-limonene and the mixture of terpene hydrocarbons obtained from the essence of oranges (e.g. cold-pressed orange terpenes and orange terpene oil phase ex fruit juice). Also useful are, for example, terpenes such as dipentene, alpha-pinene, beta-pinene and the mixture of terpene hydrocarbons expressed from lemons and grape-fruit.

Another preferred class of solvents are the C₆-C₉ alkyl aromatic hydrocarbons, especially the C₆-C₉ alkyl benzenes, in particular, octyl benzene. Short-chain alkyl benzenes (e.g. toluene) are not preferred herein due to toxicity and odor problems, and longer-chain alkyl benzenes have undesirable soil redeposition problems, especially when used to launder fabrics.

Still another preferred class of solvents are the olefins having a boiling point of at least about 100°C. The alpha-olefins have now been found to possess excellent cleaning properties and low, rather pleasant odors. The compounds 1-decene and 1-dodecene are especially preferred olefin solvents for laundry detergent use.

In a highly preferred mode, the relatively non-polar solvents, such as paraffin, olefin, terpene or alkyl benzene solvents mentioned above, are used in combination with a more polar solvent such as, for example, benzyl alcohol, n-hexanol, phthalic acid esters such as dimethyl-, diethyl-(preferred), dipropyl- or dibutyl-phthalate, or the "Carbitol" solvents such as Butyl Carbitol (trade mark for 2-(2-butoxyethoxy)ethanol)

to provide broad-spectrum cleaning of a variety of polar and non-polar soils. Such mixtures will have a ratio of non-polar:polar solvent in the range of 10:1 to 1:10, preferably 5:1 to 1:5, and most preferably have a bit more non-polar than polar solvent, generally a ratio of 5:1 to 5:4, especially for fabric laundering.

The examples disclosed hereinafter describe various other solvents which can be used in the present compositions.

As will be seen from the following disclosure, various conventional detergent ingredients are used herein at conventional amounts and concentrations.

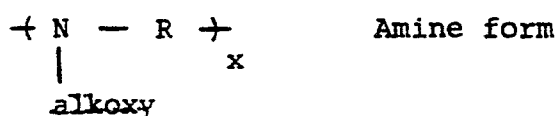
Importantly, in the formulation of liquid detergents, the solvents herein can be used in combination with relatively high (15%-25%, and higher depending on solvent) levels of fatty acid/soap, which provide an important detergency builder function.

Deterstive Surfactants - The compositions of this invention will typically contain organic surface-active agents ("surfactants") to provide the usual cleaning benefits associated with the use of such materials.

Deterstive surfactants useful herein include well-known synthetic anionic, nonionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfonates, alkyl- and alkylether sulfates, paraffin sulfonates, olefin sulfonates, alkoxyated (especially ethoxyated) alcohols and alkyl phenols, amine oxides, α -sulfonates of fatty acids and of fatty acid esters, and the like, which are well-known from the detergency art. In general, such deterstive surfactants contain an alkyl group in the C_9 - C_{18} range; the anionic deterstive surfactants can be used in the form of their sodium, potassium or triethanolammonium salts but it is to be understood that the presence of magnesium cations in the compositions usually means that at least some portion of the anionic surfactant will be in the magnesium salt form; the nonionics generally contain from about 5 to about 17 ethylene oxide groups. U.S. Patents 4 111 855 and 3 995 669 contain detailed listings of such typical deterstive surfactants, C_{11} - C_{16} alkyl benzene sulfonates, C_{12} - C_{18} paraffin-sulfonates and alkyl sulfates, and the ethoxyated alcohols and alkyl phenols are especially preferred in the compositions of the present type.

The surfactant component can comprise as little as 1% of the compositions herein, but preferably the compositions will contain 1% to 40%, preferably 10% to 40%, of surfactant. Mixtures of the ethoxyated nonionics with anionics such as the alkyl benzene sulfonates, alkyl sulfates and paraffin sulfonates are preferred for through-the-wash cleansing of a broad spectrum of soils and stains from fabrics. Such surfactants and mixes typically have HLB's of 20 and above.

Polyamines - Polyamine materials are optional ingredients in the present compositions by virtue of their ability to co-act with the solvent to remove the solid material that is present in many greasy stains (e.g., carbon black in motor oil stain; clay and color bodies in cosmetic stain). It is to be understood that the term "polyamines" as used herein represents generically the alkoxyated polyamines, both in their amine form and in their quaternarized form. Such materials can conveniently be represented as molecules of the empirical structures with repeating units:

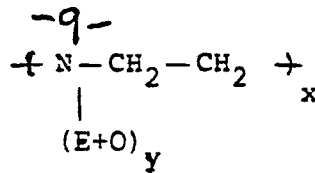


and



wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R' may be a C₁-C₂₀ hydrocarbon; the alkoxy groups are polyethoxy, polypropoxy, and the like, with polyethoxy having a degree of polymerization of 2-30, most preferably 10 to 20; x is an integer of at least 2, preferably from 2-20, most preferably 3-5; and X[⊖] is an anion such as halide or methylsulfate, resulting from the quaternization reaction. The anion X[⊖] is of no particular consequence to performance of the polyamine in the present context, and is mentioned only for completeness in the above formula.

The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene imines, i.e., the polymerized reaction product of ethylene oxide with ethyleneimine, having the general formula:



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wherein x is an integer of 3 to 5 and y is an integer of 10 to 20.

Polyamines typically will comprise at least about 0.2% of the preferred compositions herein, generally 0.5%-5%.

Other Optional Ingredients - The compositions herein can contain other ingredients which aid in their cleaning performance. For example, it is highly preferred that through-the-wash detergent compositions contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well-known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, water-soluble phosphates such as tri-polyphosphate and sodium ortho- and pyro-phosphates, silicates, and mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino-polyphosphonates and phosphates (DEQUEST) and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent 3,579,454 for typical examples of the use of such materials in various cleaning compositions. In general, the builder/sequestrant will comprise about 0.5% to 15% of the composition. Citrate is one of the most preferred builders since it is readily soluble in the aqueous phase of heavy-duty liquid detergent compositions. Such ingredients are also useful in hard-surface cleaners.


A source of magnesium ions can be used in the compositions, to assist grease removal. Besides magnesium hydroxide, water-soluble salts such as magnesium chloride, acetate, sulfate, and the like, can be used.

The laundry compositions herein also preferably contain enzymes to enhance their through-the-wash cleaning performance on a variety of soils and stains. Amylase and protease enzymes suitable for use in detergents are well-known

in the art and in commercially available liquid and granular detergents. Commercial deterative enzymes (preferably a mixture of amylase and protease) typically function best at pH above about 7 and are typically used at levels of 0.001% to 2%, and higher, in the present compositions. Ingredients such as propane diol and/or formate and calcium can be added to help stabilize the enzymes in well-known fashion, according to the desires of the formulator.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents and the like. Such ingredients typically comprise 0.1 % - 10 % of the formulations.

Water or water-alcohol (e.g., ethanol, isopropanol, etc.) mixtures are used as the carrier vehicle, and alkylated polysaccharides can be used to increase the stability and performance characteristics of the compositions.



The following examples describe a variety of formulations which can be prepared in the manner of the present invention. The examples are given by way of illustration and are not intended to be limiting of the scope of the invention. In the polyamine-containing formulations listed, the terms "x" and "y" are stated in parentheses to designate the degree of polymerization and degree of alkoxylation of the polyamine. For some "polyamines", the designation R' is also included, thereby denoting a quaternarized polyamine. For such quaternarized materials, the resulting anion X⁻ is of no consequence to cleaning performance, and is not designated.

Heavy-Duty Liquid Detergents

Special attention is directed to highly preferred formulations which are particularly useful as heavy duty liquid detergents that are suitable for laundering all manner of fabrics in a typical home laundering operation. The heavy duty liquid detergents disclosed hereinafter are formulated with a variety of deterative ingredients to provide excellent cleaning of a wide variety soils and stains, with particularly noteworthy benefits with regard to cosmetic and dirty motor oil stains.

It is to be understood that the following formulations are in the form of oil-in-water emulsions (wherein the solvent is considered the "oil" phase) and are substantially clear, homogeneous, stable microemulsions. Surprisingly, when used in a pre-treatment mode, the oil-in-water microemulsions herein are comparable in grease-cutting performance to water-in-oil emulsions, which have much higher concentrations of solvent. The compositions also exhibit excellent whiteness maintenance on cotton fabrics, apparently because the solvent reduces fatty acid soap build-up on fabric surfaces and the pH of the composition enhances enzyme cleaning performance. These performance advantages are particularly noticeable after multi-cycle washings.

The preparation of stable, heavy-duty liquid detergents in their preferred oil-in-water microemulsion form is carried-out with attention being given to the water carrier liquid, the use of fatty acid/soap as a detergency builder/emulsion stabilizer ingredient and proper attention to pH regulation.

Fatty Acids and Soaps - Fatty acids such as lauric, myristic, palmitic, stearic and oleic acids, and poly-unsaturated fatty acids, as well as their water-soluble salts (i.e., "soaps") are employed in the present compositions to provide clear, homogeneous formulations containing the solvent and water. Mixtures of fatty acids (or soaps) such as palm oil acids, coconut oil acids, and the like, in the C_{12} - C_{18} carbon chain length, can be used. In general, the concentration of fatty acid (or soap) is from 5 % to 50 %, preferably 5 % to 35 %, most preferably 10 % to 30 %, and the weight ratio of fatty acid (or soap):solvent is generally in the range of 4:1 to 1:4, preferably 3:1 to 1:2. When using fatty soap, the potassium salt and sodium forms are preferred, but any convenient water-soluble salt may be used.

Apart from their function as microemulsion stabilizers, these fatty acid/soap materials provide an important detergency builder function in the present compositions. However, it has now been discovered that when formulating oil-in-water microemulsion compositions at a pH greater than about 6.5, the presence of fatty acid/soap can actually destabilize the system. Means for overcoming this de-stabilization while maintaining a pH of 6.5 or above in microemulsions containing builder levels of fatty acid/soap are disclosed in detail, hereinafter.

Water - The liquid compositions herein may properly be characterized as "water-based", in contrast with organic solvent-based cleaners known in the art.

Surprisingly, water can interfere with the ability of solvents to remove greasy stains from fabrics. For example, a fabric stained with motor oil and dampened with water prior to treatment with a terpene solvent is not very well de-greased, if at all. By contrast, the present compositions wherein the solvents are microemulsified in water are excellent greasy stain removers when used directly on dry or damp fabrics.

Apart from water's obvious environmental and safety pedigrees and low cost as opposed to organic solvents, water-based heavy duty liquid detergents offer ease-of-formulation advantages with respect to ingredients such as most detergency builders, sanitizers, chelants, soil-suspending agents, pH-control agents, and the like, which are usually water-soluble.

Accordingly, the compositions herein exhibit the advantages of water-based formulation flexibility, together with the superior grease removal qualities of solvent-based compositions.

As will be described more fully hereinafter, the present compositions generally comprise from 10 % to 70 %, preferably 20 % to 50 % water. The weight ratio of water:solvent is generally 10:1 to 1:1, preferably 5:1 to 2:1.

pH/Stabilizer - As is well-known in the detergency arts, it is preferred for detergent compositions to be used in the near-neutral to alkaline pH range, i.e., pH 6.5, and above. This is for a variety of reasons. For example, many soils are partly peptized or emulsified by alkalinity, itself. And, many commercially available detergents (e.g., the "alkaline proteases") function optimally in alkaline laundering liquors.

It has now been discovered that stable oil-in-water microemulsion detergent compositions which comprise builder levels of fatty acid/soap are de-stabilized when their "as-is" pH

is adjusted to about 6.5, and above. (The pH where instability is noted may vary slightly with the actual grease-cutting solvent used in the microemulsion, its level, and the chain length and degree of unsaturation of the fatty acid.) This problem is especially acute with substantially non-polar, hydrocarbon grease-cutting solvents, e.g., alkyl benzenes and alpha-olefins, and liquid paraffin solvents.

The stability problem seems to arise by virtue of the fatty acid, which has an HLB of approximately 2, being converted almost entirely to soap, with an HLB of about 20, over a very narrow pH range, roughly 6.5-6.9. Thus, since the fatty acid is present in substantial amounts (ca. 5%, and higher) this major shift in HLB upsets the HLB of the emulsification system and results in de-stabilization.

It is to be understood that formulation stability could theoretically be achieved by proper selection of surfactants (discussed hereinafter) with low HLB's. For example, nonionic surfactants such as C₁₄₋₁₅ alcohols with low ethoxylate numbers (1-3) could be used. However, such low HLB surfactants do not function well as deterative surfactants, and the object herein is not only to provide stable microemulsions, but also good pre-treat and through-the-wash detergency.

It has now been found that by either increasing the ionic strength of the aqueous phase, or by adding solvent-soluble ingredients with low HLB's, which increase solvent polarity, to the solvent phase, or by using both means conjointly, the microemulsion is stabilized.

In particular, adding water-soluble, high ionic strength ingredients such as, for example, formate, sulfate, citrate, and the like, increases stability. By contrast, adding water-soluble, low ionic strength materials such as ethanol has no stabilizing effect.

Also, adding slightly polar but solvent-soluble ingredients with low HLB's such as n-hexanol, benzyl alcohol, diethyl phthalate and the like increases stability.

Conjointly adding the ionic strength ingredients and the solvent-soluble ingredients further enhances stability. Of course, the formulator can select ingredients with a view towards not only increasing microemulsion stability, but also providing optimal cleaning benefits. For example, one can choose citrate as an ionic strength agent which also has detergency builder properties, formate as an ionic strength agent which also stabilizes detergent enzymes, and n-hexanol or benzyl alcohol or diethyl phthalate as a low HLB ingredient which also serves a useful co-solvent cleaning function.

The amount of ionic strength or low e.g. (2-5) HLB solvent-soluble ingredients, or both, used in the compositions will depend somewhat on the pH desired, the concentration of fatty acid, the level of grease-cutting solvent, the composition of the deterative surfactant system, and the like. Microemulsion stability can be monitored rather simply since the true microemulsions are clear, but turn hazy and non-homogeneous, with eventual phase separation at the point of instability. Moreover, true oil-in-water microemulsions turn hazy when diluted with water, whereas water-in-oil emulsions tend to gel, and micellar oil-plus-water systems remain clear.

With regard to pH adjustments in the compositions up to about pH 6.5-6.6, any of the well-known base materials can be used, for example, triethanolamine, alkali metal hydroxide and the like. Potassium hydroxide is preferred over sodium hydroxide, inasmuch as the ease of formulation of stable systems is increased substantially by the potassium cation.

Nitrogen-functional Stabilizers/pH Regulants - It has now been discovered that various alkyl and cyclo-alkyl amines, quaternary ammonium compounds and amine oxides constitute a highly preferred class of pH regulants and stabilizers in the oil-in-water microemulsion detergent compositions of the

present type. Apparently, such materials may somehow associate with the fatty acid or anionic surfactants to form a complex which stabilizes the microemulsified oil (solvent). While the nitrogen functional compounds do not boost the pH very much towards the alkaline range (only several tenths of a pH unit, measured on the product formulated "as is") the resulting boost in detergency performance is substantial.

Diocetyl dimethyl ammonium chloride is a highly preferred quaternary used herein as a pH-regulant, but there can also be mentioned the following quaternaries in increasing order of preference of use : coconut trimethyl ammonium chloride (6.66) ; di-coconut dimethyl ammonium chloride (6.84) ; coconut benzyl dimethyl ammonium chloride (6.84) ; and dihexyl dimethyl ammonium chloride (6.89). The numbers in parentheses denote the pH achievable by adding the respective quaternaries to a liquid oil-in-water microemulsion containing fatty acid and formulated at an "as is" pH of 6.5. For the preferred dioctyl dimethyl ammonium chloride, the pH figure is 6.94.

Suitable alkyl and cyclo-alkyl amines useful herein (with attendant pH's) include : coconutalkyl diethanol amine (6.65) ; coconutalkyl dimethyl amine (6.75) ; trioctyl amine (7.0) ; and cyclohexyl amine (7.5).

Suitable amine oxides herein include coconutalkyl dimethylamine oxide (6.7) and dioctyl methylamine oxide (est. > 7).

It is to be understood that the foregoing nitrogen compounds are added to the compositions until the desired pH is obtained. To achieve the pH listed, from 0.5% to 5% of the compounds are typically used in the compositions. Cyclohexyl amine (1-5%) is most preferred for use herein.

The highly preferred, fully-formulated compositions herein are in liquid form, which can be prepared by simply blending the essential and optional ingredients in the aqueous carrier. Microemulsion stability can be estimated visually by watching for phase separation, or can be monitored more quantitatively by standard turbidometric

techniques.

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In one process aspect, the compositions can be used to pre-treat soiled fabrics by rubbing a few milliliters of the composition directly onto and into the soiled area, followed by laundering, in standard fashion. In a through-the-wash mode, the compositions are typically used at a concentration of at least 500 ppm, preferably 0.1 % to 1.5 % in an aqueous laundry bath at pH 6.5 and above to launder fabrics. The laundering can be carried out over the range from 5° C to the boil, with excellent results.

For use on hard surfaces, as rug cleaners, and as general-purpose cleaners, such compositions are usually diluted with water.

The following Examples illustrate the practice of this invention, but are not intended to be limiting thereof.



EXAMPLE I

<u>INGREDIENT</u>	<u>% By Weight</u>
C ₁₁₋₈ Alkyl Benzene Sulphonic Acid	10.0
C _{14/15} Alkyl Ethoxylate (EO 7)	10.9
Coconut Fatty Acid (Broad Cut)	18.2
Oleic Acid	2.3
Monomethyl Ethanolamine	5.8
n-Octyl Benzene	9.1
Ethanol (95 %)	2.7
DEQUEST (50 %) ^{1.}	1.09
Formic Acid	0.18
K ₃ Citrate.H ₂ O (63.5% in H ₂ O)	4.4
CaCl ₂ .2H ₂ O	0.05
Maxatase Enzyme (Protease)	0.73
Termamyl Enzyme (amylase)	0.10
Ethoxylated Polyamine ^{2.}	1.73
Perfume/Optical Brightener/Dye	0.5
Water	Balance
Product pH "as is"	6.6
Dioctyl Dimethyl Ammonium Chloride	to pH 6.94
1. Diethylene triamine pentamethylenephosphonic acid.	
2. Tetraethylene Pentamine 105 EO units/molecule	

The composition of Example I is a stable, oil-in-water microemulsion suitable for use as a laundry detergent.

EXAMPLE II

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The composition of Example I is modified by replacing the n-octyl benzene by the same amount (9.1 % total formulation) of 1-decene. Product pH "as is" : 6.6. The pH is adjusted to 6.94 with dioctyl dimethyl ammonium chloride.

EXAMPLE III

The composition of Example I is modified by replacing the n-octyl benzene by any of the following solvent mixtures (percentages of total formulation being specified in parentheses): 1-Decene (6.1 %) Diethylphthalate (3.0 %); 1-Dodecene (7.3 %)/Benzyl alcohol (1.8 %) ; n-octyl benzene (6.2 %)/Diethylphthalate (2.9 %) ; octyl benzene (6.0 %)/Butyl Carbitol (3.1 %). Product pH's as is : 6.6 In each instance, product pH is adjusted to 6.9 with dioctyl dimethyl ammonium chloride.

EXAMPLE IV

The compositions of Example III comprising solvent mixtures are adjusted to pH 7.0 with trioctyl amine and to pH 7.1 with dioctyl methylamine oxide, respectively, and stable, microemulsions are secured.

As can be seen from the foregoing, the present invention provides effective means whereby microemulsions comprising fatty acid/soap at high levels can be adjusted to a preferred pH range of 6.65 to 7.3 using mono- and di- C₆-C₁₈ tri- and dimethyl ammonium salts ; or C₄-C₈ alkyl or cycloalkyl amines; or mono- and di- C₆C₁₈ alkyl dimethyl and monomethyl amine oxides.

Further examples of the compositions herein are as follows.

EXAMPLE V

The composition of Example I is modified by replacing the Ethoxylated Polyamine with any of the following alkoxyated polyamines A, B or C, having the general formula disclosed hereinbefore.

Polyamine A : x = 2; y = 2; R = ethylene; alkoxy = ethoxy

Polyamine B : x = 20; y = 30; R = propylene; alkoxy = propoxy

Polyamine C : x = 3; y = 15; R = ethylene; alkoxy = ethoxy; R' = butyl

The alkoxyated polyamines contribute to the clay soil removal performance of the compositions.

EXAMPLE VI

The pH of the compositions of Example V are adjusted to 7.3 with addition of 5 parts (by weight of composition) of cyclohexyl amine.

EXAMPLE VII

The composition of example II is modified by replacing the 1-Decene by a mix of 6 % diethylphthalate/2 % liquid iso-paraffin/2 % orange terpene . The product is stable at pH 6.94 when dioctyl dimethyl ammonium chloride is present at a level of about 2.5 %.

Another preferred olefin solvent herein by virtue of its relatively low odor is the so-called "P-4" polymer, available from a number of petrochemical suppliers to the detergent industry as a raw material for branched alkyl benzene. P-4 is an isomer mix of the condensation product of 4 moles of propylene, i.e., C₁₂ branched olefins. P-4 is non-polar, and is preferably used in combination with a polar solvent such as benzyl alcohol, diethylphthate, Butyl Carbitol or the like.

Other useful polar solvents herein include the "Cellosolves" e.g. alkoxy alkanols such as 2-butoxyethanol ; C₆-C₁₂ alkanols (including benzyl alcohol) such as dodecanol, phenethyl alcohol, diglycoether acetates, and the like.

EXAMPLE VIII

Other solvent mixtures useful herein are as follows.

<u>Composition</u>	<u>Ingredient</u>	<u>Percent</u>
A	Octyl benzene	70%
	Diethyl phthalate	30%
B	1-Decene	70%
	Diethyl phthalate	30%
C	Octyl benzene	80%
	Benzyl alcohol	20%
D	n-Octyl benzene	90%
	Butyl carbitol	10%
E	1-Decene	65%
	Dibutyl phthalate	35%
F	n-Octyl benzene	30%
	1-Decene	40%
	Benzyl alcohol	10%
	Butyl carbitol	20%
G	1-Decene	80%
	n-Hexanol	20%
H	1-Decene	60%
	Diethyl phthalate	40%
I	1-Dodecene	80%
	Hexyl cellosolve	20%
J	Mixed 1:1 nonyl/hexyl benzene	35%
	2-Dodecene	35%
	Dimethyl phthalate	30%

In a preferred method of use aspect, the compositions herein are used in an aqueous laundering liquor, preferably at a liquor pH of 6.5-8.0 (measured as 1% of composition in water) to launder fabrics. Excellent cleaning is attained by agitating fabrics in such liquors especially at this preferred in-use pH range.

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EXAMPLE IX

A highly preferred liquid laundry detergent by virtue of the low odor properties of its grease removal solvent system, its stability in microemulsion form, and its enzymatic cleaning activity (by virtue of its pH) is as follows.

<u>Ingredient</u>	<u>Parts by Weight</u>
Alkyl(C _{11,8})benzene sulfonic acid	11.0
Alkyl(C _{14/15})ethoxylate (EO7)	12.0
Topped whole cut coconut fatty acid (1)	20.5
C ₁₀₋₁₁ isoparaffins	4.0
Diethyl phthalate	6.0
Cyclohexylamine	2.0
Monomethyl ethanolamine (2)	4.3
Potassium citrate monohydrate (63.5% in water)	2.4
Dequest 2060 S	1.7
Ethoxylated polyamine (x=5, y=15)	1.5
Ethanol	3.0
Potassium hydroxide (50% in water) (2)	3.0
Formic acid	0.2
CaCl ₂ 2H ₂ O	0.05
Optical brightener (anionic)	0.18
Maxatase enzyme (3)	0.71
Termamyl 300L enzyme (4)	0.10
Dye	20 ppm
Perfume	0.5
Water	up to 110 parts
Product pH	6.9

- (1) Chain length mixture: C₁₀(5%) C₁₂(55%) C₁₄(22%)
C₁₈(2%) oleic(10%)
- (2) To adjust pH to 6.6
- (3) From KNGS
- (4) From NOVO

The composition of Example IX is used in an aqueous laundry bath at a concentration of 100ml/10 liters and provides an in-use pH of about 7.2 (varies with water hardness).

As can be seen from the foregoing, the primary amines are preferred pH-adjusting agents herein. In general, the C₄-C₁₈ alkyl amines are used, since the lower molecular weight amines tend to be excessively malodorous. Other examples of amines useful herein include dibutyl- and di-isobutyl amine. For typical use in detergent compositions intended for home-use, amines having a boiling point above 100°C are preferred.

Product "as is" pH is measured at ambient (23°C) temperature using a commercial pH meter. The electrode is immersed in the product and the meter is allowed to stabilize before reading.

CLAIMS

1. A detergent composition in the form of a liquid oil-in-water microemulsion, wherein said oil is one or more non-polar or polar "grease-removal" solvents, said composition typically comprising from 10% to 70% water; from 5% to 20% grease removal solvent or solvent mixture; from 5% to 35% fatty acid or fatty acid/soap mixture; from 1% to 40% deterative surfactant, as well as optional deterative ingredients, said composition being characterized in that it comprises a sufficient quantity of an amine, a quaternary ammonium salt or an amine oxide to provide a pH of said composition (undiluted) above 6.5.
2. A composition according to Claim 1 wherein the amine is selected from alkyl or cyclo-alkyl amines and the pH is in the range of 6.65 to 7.5.
3. A composition according to Claim 2 wherein the amine is selected from coconut diethanol amine ; coconut alkyl dimethyl amine; trioctyl amine; dibutyl amine, disobutyl amine and cyclohexyl amine.
4. A composition according to Claim 1 wherein the quaternary ammonium salt is selected from mono- and di- C_8-C_{18} tri- and di-methyl ammonium salts.
5. A composition according to Claim 4 wherein the quaternary ammonium salt is selected from coconutalkyl trimethyl ammonium chloride, dicoconutalkyl dimethyl ammonium chloride, dihexyl dimethyl ammonium chloride and dioctyl dimethyl ammonium chloride.
6. A composition according to Claim 1 wherein the amine oxide is selected from the mono- and di- C_6-C_{18} alkyl dimethyl and monomethyl amine oxides.

7. A composition according to Claim 6 wherein the amine oxide is selected from coconutalkyl dimethyl amine oxide and dioctyl methyl amine oxide.

8. A composition according to any of claims 1-7 wherein the deterative surfactant is selected from alkyl benzene sulfonates, paraffin sulfonates alkyl sulfates, ethoxylated alcohols or alkyl phenols, or mixtures thereof.

9. A composition according to any of Claims 1-8 wherein the solvent is selected from : C₆-C₉ alkyl benzenes; liquid olefins having a boiling point of at least 100°C; terpene hydrocarbons, C₆-C₁₂ alcohols, paraffins, and mixtures thereof.

10. A composition according to any of claims 1-9 wherein the solvent is selected from a mixture of:

- a) n-octyl benzene, 1-decene, 1-dodene, liquid C₁₀ iso-paraffin or terpene; and
- b) benzyl alcohol, diethylphthalate, dibutylphthalate, or 2-(2-Butoxyethoxy)ethanol

at a weight ratio of (a) to (b) of 10:1 to 1:10.

11. A composition according to Claim 10 which contains 0.5%-5% cyclohexylamine.

12. A composition according to any of Claims 1-11 which also contains a deterative enzyme.

13. A method of laundering fabrics by agitating fabrics in an aqueous liquor containing a composition according to any of Claims 1-12 at a liquor pH of 6.5-8.0.



European Patent
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EUROPEAN SEARCH REPORT

0160762
Application number

EP 84 30 5319

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP-A-0 040 882 (PROCTER & GAMBLE CO.) * Claims 1-4 *		C 11 D 7/50 C 11 D 17/00
A	DE-C-2 823 936 (G. LIEBERWIRTH) * Claim *		
A	DE-A-1 696 130 (HENKEL & CIE.) * Page 4, paragraph 4; claim 1 *		
A	EP-A-0 021 149 (INTERNATIONAL BUSINESS MACHINES CORP.) * Claims 1-3 *		
A	EP-A-0 105 063 (PROCTER & GAMBLE CO.) * Claims 1-6 *		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 11 D 7/00 C 11 D 17/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 01-07-1985	Examiner SCHULTZE D
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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