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(54) **Liquid detergents with solvent.**

(57) Liquid detergent compositions are prepared from conventional detersive surfactants and other conventional detergent ingredients plus a grease-cutting solvent. The compositions contain fatty acids or soaps as a detergency builder and are formulated as stable oil-in-water microemulsions.

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LIQUID DETERGENTS WITH SOLVENT

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Technical Field

The present invention relates to compositions and processes for laundering fabrics which employ high levels of solvent to enhance the removal of greasy soils and stains. The liquid compositions herein are provided in the form of clear, or substantially clear, homogeneous, stable emulsions which not only provide excellent pre-treatment cleaning performance, but also exhibit improved detergency and fabric whiteness maintenance when used in an aqueous laundry liquor. In addition to providing improved removal of greasy stains, such as motor oil, cosmetics, and the like, the compositions herein also are excellent for removing particulate soils from fabrics. The compositions are formulated and stabilized at a pH in the range near neutrality to alkaline.

Background

Various organic solvents, including 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 non-

ionic 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 detersive ingredients.

Citrus juices, which contain relatively low amounts of terpenes, have been suggested for use in hand soaps and dish-washing liquids. U.S. Patent 3,650,968, 1972; Mémoire descriptif 873,051 (relating to Brevet Anglais 53472/77, 22 December 1977).

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.

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).

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 have now been found to provide

additional cleaning benefits over and above those provided by detersive 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.

Moreover, low (Ca. 3%) of terpenes, alone, in detergent compositions used in a through-the-wash mode give little in the way of additional cleaning benefits, since dilution by the wash liquor obviates their effect.

The present invention provides fully-formulated heavy duty liquid laundry detergents 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 modes.

Importantly, means are disclosed which allow such compositions to be formulated as stable microemulsions at pH's of about 6.5, and higher.

Summary of the Invention

The compositions herein may be succintly described as heavy duty liquid detergents which comprise conventional detergent ingredients such as detergency builders, enzymes, detersive surfactants, enzyme stabilizers, and the like, formulated as an oil-in-water emulsion(the solvent being the "oil" phase) in an aqueous medium, and characterized in that the compositions comprise at least 5% by weight (preferably 5-50%; more preferably 5-20%) of solvent (such as orange terpene or d-limonene, iso-paraffin oils or octyl benzene), said solvent being microemulsified in the composition by a combination of fatty acid or soap (preferably C_{12}-C_{18} fatty acid or fatty acid soap) and detersive surfactant, said composition being stabilized by proper selection of ionic strength and/or

surfactant HLB, or (preferably) nitrogen functional compound, whereby a clear, or substantially clear, stable homogeneous liquid at pH's of 6.5 and higher is provided.

Detailed Description of the Invention

The essential solvent, fatty acid (or soap) and water emulsification system, the detersive surfactant components, the means for stabilizing the formulations 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 specification 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 drycleaning industry, in the hard-surface cleaner industry and the metalworking industry. Typically, such solvents comprise hydrocarbon or halogenated hydrocarbon moieties of the alkyl or cycloalkyl 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.

Excellent solvents for use herein are the 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 mixtures 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 grapefruit.

Various other solvents and, especially, preferred mixtures of non-polar and polar solvents, which can be used in the present compositions are disclosed hereinafter.

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) including palm oil acids, coconut oil acids, and the like, in the C12-C18 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 5% to 30%, and the weight ratio of fatty acid(or soap):solvent is in the range of 4:1 to 1:4, preferably 3:1 to 1:2. When using fatty soap, the potassium and sodium salt 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 deter-

gency 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 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 such as terpenes to remove greasy stains from fabrics. For example, a fabric stained with motor oil and dampened with water prior to treatment with neat terpene is not very well de-greased by the terpene, if at all. By contrast, the present compositions wherein non-polar solvent such as the terpenes 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 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 detersive enzymes (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 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., orange terpenes and paraffin oils.

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 C_{14-15} alcohols with low ethoxylate numbers (1-3) could be used. However, such low HLB surfactants do not function well as detersive 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 ingredients with low HLB's that dissolve in the non-polar solvent, such as n-hexanol, benzyl alcohol, mixed fatty alcohols 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 as a low HLB ingredient which also serves a useful grease-cutting 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 detersive 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.

With regard to pH adjustments in the compositions, any of the well-known base materials can be used to adjust pH to about 6.5-6.6; 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.

Magnesium hydroxide is another useful neutralizing base. During use, the magnesium cation is believed to associate with anionic surfactants present in the compositions to enhance their grease-removal performance.

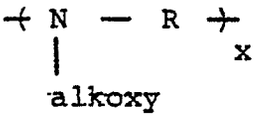
The preferred use of various amines, amine oxides and quaternary ammonium compounds (i.e.,"nitrogen-functional" compounds) to adjust the pH above 6.5-6.6 and further help stabilize the microemulsions is described in more detail, hereinafter.

Detersive 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.

Detersive 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, alkoxylated (especially ethoxylated) 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 detersive surfactants contain an alkyl group in the C_9-C_{18} range; the anionic detersive 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 detersive surfactants. C_{11}-C_{16} alkyl benzene sulfonates, C_{12}-C_{18} paraffin-sulfonates and alkyl sulfates, and the ethoxylated alcohols and alkyl phenols are especially preferred in the compositions of the present type.

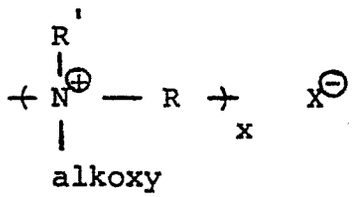
The surfactant component can comprise as little as 1% of the compositions herein, but preferably the compositions will contain 1% to 40%, preferably 10% to 40%, of surfactant. Mixtures of the ethoxylated nonionics with anionics such as the alkyl benzene sulfonates, alkyl sulfates and paraffin sulfonates 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 alkoxylated 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:



Amine form

and



Quaternarized form

wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R' may be a C_1-C_{20} 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 $X^{\ominus}$ is an anion such as halide or methylsulfate, resulting from the quaternization reaction. The anion $X^{\ominus}$ 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 ethylene-imine, having the general formula:

$$+ N - CH_2 - CH_2 +_x$$
$$\quad\quad |$$
$$\quad (E+O)_y$$

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, for the reasons stated hereinabove. 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 detersive enzymes (preferably a mixture of amylase and protease) 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 ———————— perfumes, dyes, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents and the like at levels of 0.1-15%.

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 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.

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, the compositions are diluted with water, or used full-strength, all in standard fashion.

Industrial Application

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 detersive 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. These performance advantages are particularly noticeable after multi-cycle washings.

EXAMPLE I

INGREDIENT	PARTS BY WEIGHT
Ethanol	3.0
Potassium hydroxide (50% in water)	10.0
Alkyl ($C_{11.8}$) benzene sulphonic acid	11.0
Alkyl ($C_{14/15}$) ethoxylate (EO7)	15.0
Potassium citrate monhydrate (63,5% in water)	4.8
Dequest* 2060 S (TM)	1.2
Sodium formate (40% in water)	2.5
Ca^{++} as $CaCl_2$ $6H_2O$	60 ppm
Orange Terpenes	10.0
Lauric / myristic acid (60/40)	12.5
Oleic acid	2.5
Maxatase** (TM) enzyme	0.71
Termamyl*** (TM) enzyme	0.10
FWA	0.23
Perfume	0.5
Dye	20 ppm
Water	to 100
Product pH	7.5

* Diethylene triamine pentamethylene phosphonic acid (Monsanto)

** KNGS, supplier

*** NOVO, supplier

The above composition is prepared by blending the indicated ingredients to provide a clear, stable microemulsion. In laundry tests, particularly with a pre-treatment step, the composition gives excellent performance on a wide variety of stains, especially cosmetics and dirty motor oil.

EXAMPLE II

The composition of Example I is modified slightly by using 0.6 parts by weight of magnesium hydroxide as replacement for 2 parts of the 50 % KOH and adjusting pH to 7.5 . The resulting product is a clear, stable, homogeneous microemulsion.

EXAMPLE III

The composition of Example I and II are each modified by the addition of 1.5 parts by weight of tetraethylene pentamine ethoxylated with an average of 15 moles of ethylene oxide per nitrogen atom. The resulting composition is a clear, stable, homogeneous microemulsion at pH's above 6.9.

As another example, any of the foregoing compositions may be modified by replacing the orange terpene solvent by a mixture of deodorized paraffin oil (iso-C_{10}-C_{12}; 7.5% of the total composition) and orange terpenes (2.5 % of total composition). This change in the solvent component in no way detracts from the performance attributes of the compositions, but allows the perfumer more latitude for introducing non-citrus perfume notes. Anionic optical brightener (0.01-0.5 %) may be added, as desired.

SOLVENT SELECTION

As disclosed hereinabove, final selection of the solvent system for use in the present compositions will be dependent upon soil type and load, aesthetics (odour) etc. However, a number of criteria can be used to guide this selection. For example, the solvent should be substantially water immiscible; and, it should of course be capable of solubilizing a broad range of problem greasy soils. In this latter respect thermodynamic solubility parameters (Hansen Parameters) are useful in making the solvent selection.

Any solvent can be described by the Hansen Parameters δ_d, δ_p, δ_h: δ_d being the dispersion component; δ_p the polarity component; and δ_h the hydrogen bonding component. Likerwise, key greasy problem soils can be described by "pseudo" Hansen Parameters. In order to do this the solubility of each greasy stain in a broad range of solvents of different Hansen Parameters is first assessed. This can be done by immersing the greasy stain on a range of different fabric types (cotton, polyester cotton, acrylic) in each solvent in turn for a fixed time (say, 5 minutes) under fixed agitation. On removal, excess solvent is drained-off and the stained fabric is washed for 5 minutes in cool water containing 1% concentration of a typical liquid laundry detergent. Following final rinsing in cold water and drying, the stain removal can be assessed visually or by any other suitable technique. By proceeding in this way, those solvents giving best removal of each problem greasy stain can be identified, and thereby the range of each Hansen Parameter required for optimum removal of that particular stain can be assessed. Thus, for each stain a map of Hansen Parameters can be developed, and solvent/solvent combinations can be selected on this basis to give the target performance profile.

Although not intended to be limiting of the present invention, the above technique indicates that solvent/solvent compositions with Hansen Parameters in the

range δ_d (7 to 9), δ_h (0 to 7) δ_p (0 to 4), are key for formulating microemulsions with superior greasy stain removal performance. The solvent combination can be targeted against particular greasy stains, such as motor oil, where the optimum Hansen Parameter range is δ_d (7 to 9), δ_h (0 to 4) δ_p (0 to 3) or marker ink, where the optimum range is δ_d (7 to 9) δ_h (2 to 11), δ_p (2 to 7), or targeted more broadly against mixed stains by selecting an intermediate point in the range of Hansen Parameters.

Preferred solvents and solvent mixtures herein, especially: orange terpenes (d-limonene), paraffins (especially iso-C_{10}-C_{12}); cyclohexane; kerosene; orange terpene/benzyl alcohol; (60/40), n-paraffins (C_{12-15}) / hexanol (50/50) fall within the Hansen Parameters, as stated.

Any of the foregoing examples may be modified by replacing the solvents listed with the foregoing, especially by mixtures of terpenes or paraffin oil with benzyl alcohol, n-hexanol or 1-butanol. Preferred pH's for the heavy-duty detergents are 6.5 to 8.0, more preferably 6.6-7.3. 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.

The following examples relate to compositions within the scope of this invention with solvents that are particularly suitable in industrial, heavy-duty laundry and cleaning plants, and the like. It will be appreciated by the formulator that some of the solvents employed in such compositions may be unsuitable for general home use, due to malodors, potential for skin irritation, low flash points, and the like. However, such compositions are entirely suitable for use under properly controlled conditions by professional operators who take such matters into consideration. In Examples IV-IX, the pH is adjusted in all compositions with magnesium hydroxide, as indicated. All the other ingredients are listed as parts by weight.

INGREDIENT	IV	V	VI	VII	VIII	IX
Stoddard solvent	100	-	-	-	-	250
Trichloroethylene	-	10	-	-	-	-
Naphtha	-	-	30	-	-	-
Petroleum Ether (b.p. 80-85°C)	-	-	-	60	100	-
Mineral spirits	-	-	-	20	-	-
Benzyl alcohol	-	-	-	-	100	-
Butyl carbitol (T.M.)	-	-	-	-	-	50
Polyamine (A-F*)	5(A)	10(B)	15(C)	100(D)	20(E)	150(F)
Water	100	100	200	100	250	350
Coconut fatty acids	20	20	25	60	100	15
C_{12} alkyl benzene sulfonic acid	50	5	-	-	10	20
C_{12-15} alcohol ethoxylate (EOAvg 9)	50	-	-	-	-	20
C_9 alkyl phenol (ethoxylated EO Avg 6)	-	2	10	100	10	-
$Mg(OH)_2$ to pH shown	7.0	7.1	7.5	-	7.7	8.1

* Polyamines A-F used in Examples IV-IX have the general formulae disclosed hereinbefore and are as follows:

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

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

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

D x = 5;y = 9;R = butylene ; aloxy = butoxy

E x = 20;y = 10;R = hexylene ; aloxy = ethoxy ; R' ; dodecyl

F x = 3;y = 20;R = ethylene ; alkoxy = ethoxy ; R' = eicosyl

As can be seen from the foregoing, the present invention encompasses a variety of formulations in the form of stable, solvent-containing emulsions. A superior heavy duty liquid detergent composition can also be prepared using a solvent system comprising diethyl phthalate (preferred) or dibutyl phthalate in combination with the terpenes (preferably, orange terpene) or dipentene, or paraffin oils, or (most preferably) mixtures thereof. The following is a representative example of such a composition.

EXAMPLE X

Ingredient	Parts by weight
Polyamine (x=5;y=15)	1.5
Potassium Hydroxide (50 % Aq.)	8.0
Ethanol	3.0
$C_{11.8}$ Alkyl Benzene Sulphonic Acid	11.0
$C_{14/15}$ Alkyl Ethoxylate (E0 7)	15.0
Potassium Citrate (63.5 Aq.)	2.4
Deodorized Paraffin Oil (iso-C_{10})	7.5
Orange Terpene	2.5
Dibutyl phthalate	3.0
Lauric/Myristic Acids (60/40)	12.5
Enzymes (per Ex. X)	1.0
Water and minors with pH adjusted with Mg $(OH)_2$ to 7.3	to 100

In Example X , the dibutyl phthalate can be replaced by an equivalent amount of diethyl phthalate.

It will be appreciated that many of the foregoing compositions comprising the terpene hydrocarbons will necessarily have a rather strong citrus odor that may not be entirely acceptable to all formulators of such compositions. It has now been discovered that the C_6-C_9 alkyl aromatic solvents, especially the C_6-C_9 alkyl benzenes, preferably octyl benzene, exhibit excellent grease-removal properties and have a low, pleasant odor. Likewise, the olefin solvents having a boiling point of at least about 100°C, especially alpha-olefins, preferably 1-decene or 1-dodecene, are excellent grease-removal solvents. Also, the iso-paraffins (especially C_{10}-C_{12} chain lengths) are noteworthy for their low odor and high grease-removal characteristics.

The combination of the aforesaid alkyl-aromatic or paraffin or olefin solvents with polar liquids such as benzyl alcohol, n-hexanol, Butyl Carbitol (Trade Mark; 2-(2-butoxyethoxy) ethanol) or the phthalic acid esters constitute additional examples of preferred non-polar/polar solvents that are preferred for use in the practice of this invention.

The following additional examples further illustrate oil-in-water microemulsions. In Example XIV, the use of the quaternary ammonium compound to adjust the pH of the formulation to a pH just barely below neutrality contributes importantly to product performance while maintaining long-term microemulsion stability.

EXAMPLE XI

Ingredient	% By Weight
$C_{11.8}$ 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
1-Decene	9.1
Ethanol (95%)	2.7
Dequest (50%)[1]	1.09
Formic acid	0.18
K_3 citrate . H_2O (63.5% in H_2O)	4.4
$CaCl_2$. $2H_2O$	0.05
Maxatase enzyme (protease)	0.73
Termamyl enzyme (amylase)	0.10
Ethoxylated polyamine [2]	1.73
Perfume/optional brightener/dye	0.5
Water	Balance
Product pH	6.6

1. Diethylene triamine pentamethylenephosphonic acid
2. Tetraethylene pentamine 105 EO units/molecule

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

EXAMPLE XII

The composition of Example XI is modified by replacing the 1-Decene by the same amount (9.1% total formulation) of n-octyl benzene. Product pH "as is" : 6.6.

EXAMPLE XIII

The composition of Example XI is modified by replacing the 1-Decene 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%)/Diethyl phthalate (2.9%); n-octyl benzene (6.0%)/ Butyl carbitol (3.1%). Product pH's as is : 6.6.

EXAMPLE XIV

The compositions of Examples XI, XII, and XIII are modified by adding sufficient dioctyldimethyl ammonium chloride to adjust the "as is" pH of the compositions from 6.6 to 6.94. The resulting compositions exhibit exceptionally good fabric cleaning and whiteness maintenance.

It is to be understood that the preferred compositions of Examples XI-XIV are in the form of true oil-in-water microemulsions. On diluting with water, the compositions appear hazy. In contrast, water-in-oil emulsions tend to gel on dilution, whereas micellar oil-in-water compositions remain clear on dilution.

Example XIV illustrates the use of a nitrogen-functional ingredient (the quaternary) to adjust product pH. Other such pH adjusting agents include the following (product pH being indicated in parentheses): coconutalkyldiethanol amine (6.65); coconutdimethyl amine (6.75); trioctylamine (7.0); cyclohexylamine (7.5); coconutalkyl trimethylammonium chloride (6.66); coconutalkyl dimethylamine oxide (6.70); dicoconutalkyl dimethylammonium chloride (6.84); coconutalkyl benzyl dimethylammonium chloride (6.84); dihexyl dimethylammonium chloride (6.89); and dioctyl methyl amine oxide (> 7 est.). Such nitrogen-functional materials are used at

levels from 0.5-5% in the compositions to adjust pH, and importantly contribute to cleaning and whiteness maintenance of laundered fabrics. Cyclohexyl amine (1-5%) is preferred for this use.

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., C_{12} branched olefins. P-4 is non-polar, and is preferably used in combination with a polar solvent such as benzyl alcohol, diethylphthalate, Butyl Carbitol, or the like.

Other useful polar solvents herein besides the "Carbitols" (2-(2-alkoxyethoxy)ethanols) include the "Cellosolves", e.g. 2-alkoxyl alkanols such as 2-butoxyethanol; C_4-C_{12} alkyl alcohols, such as dodecanol, phenethyl alcohol, and the diglycolether acetates, and the like.

EXAMPLE XV

A preferred composition by virtue of its low odor qualities and compatibility with polethylene containers is prepared by replacing the 1-decene of Example XI with a solvent mixture which comprises (as percent total composition) 6% diethylphthalate/2% iso-paraffin liquid (C_{10}-C_{12})/2% orange terpene.

Importantly, all microemulsion compositions herein do not affect high density polyethylene and thus can be packaged in high density polyethylene bottles. In contrast, many solvent-containing cleaners that are not in true microemulsion form must be packaged in the more expensive metal cans or polyvinylchloride bottles.

EXAMPLE XVI

The following are further examples of grease-removal solvent mixtures of polar and non-polar solvents for use herein.

Composition	Ingredient	Percent
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 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 at this in-use pH range.

EXAMPLE XVII

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.

Ingredient	Parts by Weight
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
$CaCl_2$ $2H_2O$	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: C_{10}(5%) C_{12}(55%) C_{14}(22%) C_{18}(2%) oleic(10%)
(2) To adjust pH to 6.6
(3) From KNGS
(4) From NOVO

The composition of Example XVII 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).

The most highly preferred cleaning solvent mixtures of paraffins, especially iso-C_{10-12} (most preferably iso-C_{10}) paraffin hydrocarbons and diethyl phthalate (or, less preferred, dibutyl phthalate) function exceptionally well in cleaning fabrics, both in a pre-treatment and through-the-wash mode. These particular solvents, formulated at a ratio of 5:1 to 1:5, are especially advantageous due to their exceptionally low odor. Mixtures of these solvents with cyclohexylamine (ratio solvent mix to cyclohexyl amine 10:1 to 1:10, preferably 5:1 to 2:1) provide homogeneous liquid compositions of the oil-in-water microemulsion type that are preferred for all manner of cleaning operations where greasy stain removal is a consideration.

Besides their excellent cleaning performance, the microemulsion compositions of this invention are noteworthy for their mildness to skin. This unexpected benefit in solvent-containing compositions allows the compositions to be used in hand-washing of fine fabrics, china, glassware, and the like.

CLAIMS

1. A liquid detergent composition containing conventional detersive surfactants and other detergent ingredients, characterized in that said composition contains:

a) at least 5% of a grease-removal solvent;

b) from 5% to 50% of a fatty acid or soap;

said composition being formulated as a stable oil-in-water microemulsion at a pH of 6.5, or above.

2. A composition according to Claim 1 wherein the solvent comprises terpenes, paraffin oil, C_6-C_9 alkyl aromatics, liquid olefins, or mixtures thereof, or mixtures of terpenes, paraffin oils, C_6-C_9 alkyl aromatics or olefins, with benzyl alcohol, C_4-C_{12} alcohols, phthalic acid esters, 2-(2-alkoxyethoxy)ethanols or 2-alkoxyalkanols.

3. A composition according to Claim 2 wherein the solvent is a mixture of:

(a) a non-polar solvent selected from terpenes, iso-C_{10}-C_{12} paraffin oils, C_6-C_9 alkyl benzenes or liquid olefins; and

(b) a polar solvent selected from benzyl alcohol, diethylphthalate, dibutylphthalate or 2-(2-butoxyethoxy)-ethanol

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

4. A composition according to Claims 1 to 3 wherein the fatty acid, or fatty acid soap, is a mix of lauric and myristic fatty acids or soaps, coconutalkyl fatty acid or fatty soap mixture, or mixtures of palm and coconut fatty acids or soaps.

5. A composition according to Claims 1 to 4 which is formulated as a clear microemulsion at a pH of 6.5 to 8.0.

6. A heavy-duty liquid detergent composition in stable oil-in-water microemulsion form characterized in that it comprises:

a) from 10% to 40% of conventional detersive surfactant;

b) from 5% to 20% of grease-removal solvent;

c) from 5% to 30% of fatty acid or soap;

the balance of said composition comprising other conventional detergent ingredients and an aqueous carrier, said composition being formulated at a pH at or above 6.5.

7. A composition according to Claim 6 wherein the detersive surfactant is selected from C_9-C_{18} alkyl benzene sulfonates, paraffin sulfonates, α-sulfonate of fatty acids, alkyl sulfates, and ethoxylated alcohols and alkyl phenols having 5 to 17 ethylene oxide groups, and mixtures thereof.

8. A composition according to Claim 7 wherein the solvent is a mixture of:

(a) a non-polar solvent selected from terpenes, iso-C_{10}-C_{12} paraffin oils, C_6-C_9 alkyl benzenes or liquid olefins; and

(b) a polar solvent selected from benzyl alcohol, diethylphthalate, dibutylphthalate or 2-(2-butoxyethoxy)-ethanol

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

9. A composition according to Claim 8 wherein the fatty acid or soap is a mixture of lauric and myristic acids or soaps, coconutalkyl fatty acid or fatty soap mixture, or mixtures of palm and coconut fatty acids or soaps.

10. A composition according to Claim 9 which is formulated at a pH of 6.6 to 8.0.

11. A composition according to Claim 10 formulated at a pH of 6.6 to 7.3.

12. A composition according to any of Claims 1-11 packaged in a high density polyethylene container.

13. A method of laundering fabrics by agitating fabrics in an aqueous liquor containing a composition according to any of Claims 1-11.

14. A cleaning solvent mixture which comprises a mixture of iso-C_{10}-C_{12} paraffin and diethyl phthalate or dibutyl phthalate, at a weight ratio of paraffin:phthalate of 5:1 to 1:5.

15. The cleaning solvent mixture of Claim 14 which additionally contains cyclohexyl amine.

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EUROPEAN SEARCH REPORT

Application number
EP 84 30 5317

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)
X	EP-A-0 052 786 (IBM) * Page 5, table 1, claims 1-7 *	1	C 11 D 7/50 C 11 D 3/43 C 11 D 17/00
D,X	EP-A-0 040 882 (PROCTER & GAMBLE CO.) * Page 3, line 27 - page 4, line 30, page 5, line 26 - page 6, line 6, page 19, examples 8-13, claims 1-7 *	1-3,6, 7	
X,P	EP-A-0 106 266 (PROCTER & GAMBLE CO.) * Page 4, lines 12-31, page 5, lines 6, 7, page 5, line 26 - page 6, line 6, page 19, examples 8-13, claims 1-3 *	1-3,5-7	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 11 D 3/00
C 11 D 7/00
C 11 D 17/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	02-11-1984	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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