(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 672 747 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **95301622.7**

(22) Date of filing: **13.03.95**

(51) Int. Cl.[6]: **C11D 1/83,** C11D 3/20, C11D 3/18, C11D 17/00

(30) Priority: **14.03.94 US 209896**

(43) Date of publication of application: **20.09.95 Bulletin 95/38**

(84) Designated Contracting States: **AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE**

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(54) Microemulsion all purpose liquid cleaning compositions.

(57) An improvement is described in microemulsion compositions which is more environmentally friendly, especially effective in the removal of oily and greasy soil and has an evidenced grease release effect, contains an anionic detergent, an esterfied ethoxylated glycerol type compound, a hydrocarbon ingredient, and water which comprises the use of a water-insoluble odoriferous perfume as the essential hydrocarbon ingredient in a proportion sufficient to form either a dilute o/w microemulsion composition containing, by weight, 0.1% to 6% of an anionic detergent, 0 to 16% of a nonionic surfactant, 0.1 to 50% of a cosurfactant, 0.1% to 20% of the esterfied ethoxylated glycerol type compound, 0.4% to 10% of perfume or a hydrocarbon and the balance being water.

EP 0 672 747 A2

Field of the Invention

This invention relates to an improved all-purpose liquid cleaner in the form of a microemulsion designed in particular for cleaning hard surfaces and which is effective in removing grease soil and/or bath soil and in leaving unrinsed surfaces with a shiny appearance.

Background Of The Invention

In recent years all-purpose liquid detergents have become widely accepted for cleaning hard surfaces, e.g., painted woodwork and panels, tiled walls, wash bowls, bathtubs, linoleum or tile floors, washable wall paper, etc.. Such all-purpose liquids comprise clear and opaque aqueous mixtures of water-soluble synthetic organic detergents and water-soluble detergent builder salts. In order to achieve comparable cleaning efficiency with granular or powdered all-purpose cleaning compositions, use of water-soluble inorganic phosphate builder salts was favored in the prior art all-purpose liquids. For example, such early phosphate-containing compositions are described in U.S. Patent Nos. 2,560,839; 3,234,138; 3,350,319; and British Patent No. 1,223,739.

In view of the environmentalist's efforts to reduce phosphate levels in ground water, improved all-purpose liquids containing reduced concentrations of inorganic phosphate builder salts or non-phosphate builder salts have appeared. A particularly useful self-opacified liquid of the latter type is described in U.S. Patent No. 4,244,840.

However, these prior art all-purpose liquid detergents containing detergent builder salts or other equivalent tend to leave films, spots or streaks on cleaned unrinsed surfaces, particularly shiny surfaces. Thus, such liquids require thorough rinsing of the cleaned surfaces which is a time-consuming chore for the user.

In order to overcome the foregoing disadvantage of the prior art all-purpose liquid. U.S. Patent No. 4,017,409 teaches that a mixture of paraffin sulfonate and a reduced concentration of inorganic phosphate builder salt should be employed. However, such compositions are not completely acceptable from an environmental point of view based upon the phosphate content. On the other hand, another alternative to achieving phosphate-free all-purpose liquids has been to use a major proportion of a mixture of anionic and nonionic detergents with minor amounts of glycol ether solvent and organic amine as shown in U.S. Patent NO. 3,935,130. Again, this approach has not been completely satisfactory and the high levels of organic detergents necessary to achieve cleaning cause foaming which, in turn, leads to the need for thorough rinsing which has been found to be undesirable to today's consumers.

Another approach to formulating hard surface or all-purpose liquid detergent compositions where product homogeneity and clarity are important considerations involves the formation of oil-in-water (o/w) microemulsions which contain one or more surface-active detergent compounds, a water-immiscible solvent (typically a hydrocarbon solvent), water and a "cosurfactant" compound which provides product stability. By definition, an o/w microemulsion is a spontaneously forming colloidal dispersion of "oil" phase particles having a particle size in the range of about 25 to about 800 Å in a continuous aqueous phase.

In view of the extremely fine particle size of the dispersed oil phase particles, microemulsions are transparent to light and are clear and usually highly stable against phase separation.

Patent disclosures relating to use of grease-removal solvents in o/w microemulsions include, for example, European Patent Applications EP 0137615 and EP 0137616 - Herbots et al; European Patent Application EP 0160762 - Johnston et al; and U.S. Patent No. 4,561,991 - Herbots et al. Each of these patent disclosures also teaches using at least 5% by weight of grease-removal solvent.

It also is known from British Patent Application GB 2144763A to Herbots et al, published March 13, 1985, that magnesium salts enhance grease-removal performance of organic grease-removal solvents, such as the terpenes, in o/w microemulsion liquid detergent compositions. The compositions of this invention described by Herbots et al. require at least 5% of the mixture of grease-removal solvent and magnesium salt and preferably at least 5% of solvent (which may be a mixture of water-immiscible non-polar solvent with a sparingly soluble slightly polar solvent) and at least 0.1% magnesium salt.

However, since the amount of water immiscible and sparingly soluble components which can be present in an o/w microemulsion, with low total active ingredients without impairing the stability of the microemulsion is rather limited (for example, up to about 18% by weight of the aqueous phase), the presence of such high quantities of grease-removal solvents tend to reduce the total amount of greasy or oily soils which can be taken up by and into the microemulsion without causing phase separation.

The following representative prior art patents also relate to liquid detergent cleaning compositions in the form of o/w microemulsions: U.S. Patents Nos. 4,472,291 - Rosario; 4,540,448 - Gauteer et al; 3,723,330 - Sheflin; etc.

Liquid detergent compositions which include terpenes, such as d-limonene, or other grease-removal solvents, although not disclosed to be in the form of o/w microemulsions, are the subject matter of the following representative patent documents: European Patent Application 0080749; British Patent Specification 1603047; USP 4414128; and USP 4540505. For example, US Patent No. 4414128 broadly discloses an aqueous liquid detergent composition characterized by, by weight:

(a) from about 1% to about 20% of a synthetic anionic, nonionic, amphoteric or zwitterionic surfactant or mixture thereof;

(b) from about 0.5% to about 10% of a mono- or sesquiterpene or mixture thereof. at a weight ratio of (a):(b) lying in the range of 5:1 to 1:3; and

(c) from about 0.5% about 10% of a polar solvent having a solubility in water at 15°C in the range of from about 0.2% to about 10%. Other ingredients present in the formulations disclosed in this patent include from about 0.05% to about 2% by weight of an alkali metal, ammonium or alkanolammonium soap of a C_{13}-C_{24} fatty acid; a calcium sequestrant from about 0.5% to about 13% by weight; non-aqueous solvent, e.g., alcohols and glycol ethers, up to about 10% by weight; and hydrotropes, e.g., urea, ethanolamines, salts of lower alkylaryl sulfonates, up to about 10% by weight. All of the formulations shown in the Examples of this patent include relatively large amounts of detergent builder salts which are detrimental to surface shine.

Furthermore, the present inventors have observed that in formulations containing grease-removal assisting magnesium compounds, the addition of minor amounts of builder salts, such as alkali metal polyphosphates, alkali metal carbonates, nitrilotriacetic acid salts, and so on, tends to make it more difficult to form stable microemulsion systems.

U.S. Patent 5,082,584 discloses a microemulsion composition having an anionic surfactant, a cosurfactant, nonionic surfactant, perfume and water; however, these compositions do not possess the low ecotoxicity and the improved interfacial tension properties as exhibited by the compositions of the instant invention.

U.S. Patent 3,776,857 discloses the use of long chain fatty acid esters of ethylene oxide adducts of aliphatic polyhydric alcohols as surfactants for use in agricultural compositions.

British Patent No. 1,453,385 discloses polyesterified nonionic surfactants similar to the polyesterified nonionic compounds of the instant invention. However, these nonionic surfactants of British Patent 1,453,385 do not disclose the formula (II) portion of the instant composition. Additionally, the formulated compositions of British Patent 1,453,385 fail to disclose the critical limitations of the instant invention.

Summary of the Invention

The present invention provides an improved, clear, liquid cleaning composition having improved interfacial tension which improves cleaning hard surfaces in the form of a microemulsion which is suitable for cleaning hard surfaces such as plastic, vitreous and metal surfaces having a shiny finish. More particularly, the improved cleaning compositions exhibit good grease soil removal properties due to the improved interfacial tensions, when used in undiluted (neat) form and leave the cleaned surfaces shiny without the need of or requiring only minimal additional rinsing or wiping. The latter characteristic is evidenced by little or no visible residues on the unrinsed cleaned surfaces and, accordingly, overcomes one of the disadvantages of prior art products. The instant compositions exhibit a grease release effect in that the instant compositions impede or decrease the anchoring of greasy soil on surfaces that have been cleaned with the instant compositions as compared to surfaces cleaned with a commercial microemulsion composition which means that the grease soiled surface is easier to clean upon subsequent cleanings.

Surprisingly, these desirable results are accomplished even in the absence of polyphosphate or other inorganic or organic detergent builder salts and also in the complete absence or substantially complete absence of grease-removal solvent.

In one aspect, the invention generally provides a stable, clear all-purpose, hard surface cleaning composition especially effective in the removal of oily and greasy oil, which is in the form of a substantially dilute oil-in-water microemulsion having an aqueous phase and an oil phase; The dilute o/w microemulsion includes, on a weight basis:

0 to about 6% by weight of an anionic surfactant;

0 to about 16.0% of a nonionic surfactant;

about 0.1% to about 50% of a cosurfactant having either limited ability or substantially no ability to dissolve oily or greasy soil;

0 to about 8% of an alkali metal dialkylsulfosuccinate

about 0.1% to about 20% of a mixture of a fully esterfied ethoxylated polyhydric alcohol, a partially esterified ethoxylated polyhydric alcohol and a nonesterified ethoxylated polyhydric alcohol;

0 to about 15% of magnesium sulfate heptahydrate;

about 0.4 to about 10.0% of at least one perfume and/or water insoluble hydrocarbon; and balance being water e.g.

about 10 to about 85% of water, said proportions being based upon the total weight of the composition.

Quite surprisingly although the perfume is not, per se, a solvent for greasy or oily soil, --even though some perfumes may, in fact, contain as much as about 80% of terpenes which are known as good grease solvents -- the inventive compositions in dilute form have the capacity to solubilize up to about 10 times or more of the weight of the perfume of oily and greasy soil, which is removed or loosened from the hard surface by virtue of the action of the anionic and nonionic surfactants, said soil being taken up into the oil phase of the o/w microemulsion.

In second aspect, the invention generally provides highly concentrated microemulsion compositions in the form of either an oil-in-water (o/w) microemulsion or a water-in-oil (w/o) microemulsion which when diluted with additional water before use can form dilute o/w microemulsion compositions. Broadly, the concentrated microemulsion compositions contain, by weight, 0% to 6% of an anionic detergent, 0 to 16% of a nonionic surfactant, 0% to 8% of an alkali metal dialkylsulfosuccinate, 0.1% to 20% of a mixture of a fully esterfied ethoxylated polyhydric alcohol, a partially esterified ethoxylated polyhydric alcohol and a nonesterified ethoxylated polyhydric alcohol, 0% to 2.5% of a fatty acid, 0.4% to 10% of perfume or water insoluble hydrocarbon having about 6 to 18 carbon atoms, 0.1% to 50% of a cosurfactant, and balance being water e.g. 20% to 97% of water.

Detailed Description of the Invention

The present invention relates to a stable microemulsion composition approximately by weight: 0.1% to 6% of an anionic surfactant, 1.0 to 16% of a nonionic surfactant, 0.1% to 50% of a cosurfactant, 0% to 2.5% of a fatty acid, 0% to 8% of an alkali metal dialkylsulfosuccinate, 0.1% to 20% of a mixture of a fully esterfied ethoxylated polyhydric alcohol, a partially esterified ethoxylated polyhydric alcohol and a nonesterified ethoxylated polyhydric alcohol, 0.1% to 10% of a water insoluble hydrocarbon or a perfume and the balance being water.

The detergent compositions of the present invention are in the form of an oil-in-water microemulsion in the first aspect or after dilution with water in the second aspect, with the essential ingredients being water, anionic surfactant, esterified ethoxylated polyhydric alcohol and a hydrocarbon or perfume.

According to the present invention, the role of the hydrocarbon is provided by a water insoluble perfume. Typically, in aqueous based compositions the presence of a solubilizer, such as an alkali metal lower alkyl aryl sulfonate hydrotrope, triethanolamine, urea, etc., is required for perfume dissolution, especially at perfume levels of about 1% and higher, since perfumes are generally a mixture of fragrant essential oils and aromatic compounds which are generally not water-soluble. Therefore, by incorporating the perfume into the aqueous cleaning composition as the oil (hydrocarbon) phase of the ultimate o/w microemulsion composition, several different important advantages are achieved.

First, the cosmetic properties of the ultimate cleaning composition are improved: the compositions are both clear (as a consequence of the formation of a microemulsion) and highly fragranced (as a consequence of the perfume level).

Second, the need for use of solubilizers, which do not contribute to cleaning performance, is eliminated.

Third, an improved grease release effect and an improved grease removal capacity in neat (undiluted) usage of the dilute aspect or after dilution of the concentrate can be obtained without detergent builders or buffers or conventional grease removal solvents at neutral or acidic pH and at low levels of active ingredients while improved cleaning performance can also be achieved in diluted usage.

As used herein and in the appended claims the term "perfume" is used in its ordinary sense to refer to and include any non water-soluble fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flower, herb, blossom or plant) and artificial (i.e., mixture of natural oils or oil constituents and synthetically produced substances) odoriferous substances. Typically, perfumes are complex mixtures of blends of various organic compounds such as alcohols, aldehydes, ethers, aromatic compounds and varying amounts of essential oils (e.g., terpenes) such as from about 0% to about 80%, usually from about 10% to 70% by weight, the essential oils themselves being volatile odoriferous compounds and also serving to dissolve the other components of the perfume.

In the present invention the precise composition of the perfume is of no particular consequence to cleaning performance so long as it meets the criteria of water immiscibility and having a pleasing odor. Naturally, of course, especially for cleaning compositions intended for use in the home, the perfume, as well as all other ingredients, should be cosmetically acceptable, i.e., non-toxic, hypoallergenic, etc.. The instant compositions show a marked improvement in ecotoxicity as compared to existing commercial products.

The hydrocarbon such as a perfume is present in the dilute o/w microemulsion in an amount of from about 0.1% to about 10% by weight, preferably from about 0.4% to about 3.0% by weight, especially preferably from about 0.5% to about 2.0% by weight. If the amount of hydrocarbon (perfume) is less than about 0.4% by weight it becomes difficult to form the o/w microemulsion. If the hydrocarbon (perfume) is added in amounts more than about 10% by weight, the cost is increased without any additional cleaning benefit and, in fact, with some diminishing of cleaning performance insofar as the total amount of greasy or oily soil which can be taken up in the oil phase of the microemulsion will decrease proportionately.

Furthermore, although superior grease removal performance will be achieved for perfume compositions not containing any terpene solvents, it is apparently difficult for perfumers to formulate sufficiently inexpensive perfume compositions for products of this type (i.e., very cost sensitive consumer-type products) which include less than about 20%, usually less than about 30%, of such terpene solvents.

Thus, merely as a practical matter, based on economic consideration, the dilute o/w microemulsion detergent cleaning compositions of the present invention may often include as much as about 0.2% to about 7% by weight, based on the total composition, of terpene solvents introduced thereunto via the perfume component. However, even when the amount of terpene solvent in the cleaning formulation is less than 1.5% by weight, such as up to about 0.6% by weight or 0.4% by weight or less, satisfactory grease removal and oil removal capacity is provided by the inventive diluted o/w microemulsions.

Thus, for a typical formulation of a diluted o/w microemulsion according to this invention a 20 milliliter sample of o/w microemulsion containing 1% by weight of perfume will be able to solubilize, for example, up to about 2 to 3 ml of greasy and/or oily soil, while retaining its form as a microemulsion. In other words, it is an essential feature of the compositions of this invention that grease removal is a function of the result of the microemulsion, per se, and not of the presence or absence in the microemulsion of a "greasy soil removal" type of solvent.

In place of the perfume one can employ a water insoluble paraffin or isoparaffin having about 6 to about 18 carbon at a concentration of about 0.4 to about 8.0 wt. percent, more preferably 0.4 to 3.0 wt. %.

The water-soluble organic detergent materials which are used in forming the ultimate o/w microemulsion compositions of this invention may be selected from the group consisting of water-soluble, non-soap, anionic detergents and nonionic surfactants mixed with a mixture of a fully esterfied ethoxylated polyhydric alcohol, a partially esterified ethoxylated polyhydric alcohol and a nonesterified ethoxylated polyhydric alcohol.

The nonionic surfactant is present in the instant composition in amounts of about 0% to 16%, preferably 1% to 12%, most preferably 1.5% to 10%, by weight of the composition and provides superior performance in the removal of oily soil and mildness to human skin.

The water soluble nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates and ethylene-oxide-propylene oxide condensates of primary alkanols such as Plurafacs (BASF) and condensates of ethylene oxide with sorbitan fatty acid esters such as the Tweens (ICI). The nonionic synthetic organic surfactants generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water-soluble nonionic detergent. Furthermore, the length of the polyethenoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

The nonionic surfactant class includes the condensation products of a higher alcohol (e.g., an alkanol containing about 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with about 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with about 16 moles of ethylene oxide (EO), tridecanol condensed with about 6 to 20 moles e.g. about 6 moles of EO, myristyl alcohol condensed with about 10 moles of EO per mole of mysristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to about 14 carbon atoms in length and wherein the condensate contains either about 6 moles of EO per mole of total alcohol or about 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co,), which are higher aliphatic, primary alcohols containing about 9-15 carbon atoms, such as C_9-C_{11} alkanol condensed with 8 moles of ethylene oxide (Neodol 91-18), C_{12-13} alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C_{12-15} alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C_{14-15} alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrolpholic lipophilic balance) value of about 8-15 and give good O/W emulsification, whereas ethoxamers with HLB values below 8 contain less than 5 ethyleneoxy groups and tend to be poor emulsifiers and poor surfactants (at least for the present purpose).

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the foregoing type are C11-C15 secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

Other suitable nonionic surfactants include the polyethylene oxide condensates of one mole of alkyl phenol containing from about 8 to 18 carbon atoms in a straight-or branched chain alkyl group with about 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl phenol condensed with about 9.5 moles of EO per mole of nonyl phenol, dinonyl phenol condensed with about 12 moles of EO per mole of phenol, dinonyl phenol condensed with about 15 moles of EO per mole of phenol and isoctylphenol condensed with about 15 moles of EO per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630 (nonyl phenol ethoxylate) marketed by GAF Corporation.

Also among the satisfactory nonionic surfactants are the water-soluble condensation products of a C_8-C_{20} alkanol with a heteric mixture of ethylene oxide and propylene oxide wherein the weight ratio of ethylene oxide to propylene oxide is from 2.5:1 to 4:1, preferably 2.8:1-3.3:1, with the total of the ethylene oxide and propylene oxide (including the terminal ethanol or propanol group)being from 60-85%, preferably 70-80%, by weight. Such detergents are commercially available from BASF-Wyandotte and a particularly preferred detergent is a C_{10}-C_{16} alkanol condensate with ethylene oxide and propylene oxide, the weight ratio of ethylene oxide to propylene oxide being 3:1 and the total alkoxy content being about 75% by weight.

Condensates of 2 to 30 moles of ethylene oxide with sorbitan mono-and tri-C_{10}-C_{20} alkanoic acid esters having a HLB of 8 to 15 also may be employed as the nonionic surfactant ingredient in the described all purpose cleaner. These surfactants are well known and are available from Imperial Chemical Industries under the Tween trade name. Suitable surfactants include polyoxyethylene (4) sorbitan monolaurate, polyoxyethylene (4) sorbitan monostearate, polyoxyethylene (20) sorbitan trioleate and polyoxyethylene (20) sorbitan tristearate.

Other suitable water-soluble nonionic surfactants which are less preferred are marketed under the trade name "Pluronics". The compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion of the molecule is on the order of 950 to 4000 and preferably 200 to 2,500. The addition of polyoxyethylene radicals to the hydrophobic portion tends to increase the solubility of the molecule as a whole so as to make the surfactant water-soluble. The molecular weight of the block polymers varies from 1,000 to 15,000 and the polyethylene oxide content may comprise 20% to 80% by weight. Preferably, these surfactants will be in liquid form and satisfactory surfactants are available as grades L 62 and L 64.

Regarding the anionic surfactant present in the o/w microemulsions any of the conventionally used water-soluble anionic detergents or mixtures of said anionic surfactants and nonionic surfactants can be used in this invention. As used herein the term "anionic surfactant" is intended to refer to the class of anionic and mixed anionic-nonionic surfactants providing detersive action.

Suitable water-soluble non-soap, anionic surfactants include those surface-active or detergent compounds which contain an organic hydrophobic group containing generally 8 to 26 carbon atoms and preferably 10 to 18 carbon atoms in their molecular structure and at least one water-solubilizing group selected from the group of sulfonate, sulfate and carboxylate so as to form a water-soluble detergent. Usually, the hydrophobic group will include or comprise a C_8-C_{22} alkyl, alkenyl, or acyl group. Such detergents are employed in the form of water-soluble salts and the salt-forming cation usually is selected from the group consisting of sodium, potassium, ammonium, magnesium and mono-, di- or tri-C_2-C_3 alkanolammonium, with the sodium, magnesium and ammonium cations again being preferred.

Examples of suitable sulfonated anionic surfactants are the well known higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain. C_8-C_{15} alkyl toluene sulfonates and C_8-C_{15} alkyl phenol sulfonates.

A preferred sulfonate is linear alkyl benzene sulfonate having a high content of 3- (or higher) phenyl isomers and a correspondingly low content (well below 50%) of 2- (or lower) phenyl isomers, that is, wherein the benzene ring is preferably attached in large part at the 3 or higher (for example, 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Particularly preferred materials are set forth in U.S. Patent 3,320,174.

Other suitable anionic surfactants are the olefin sulfonates, including long-chain alkene sulfonates, long-chain hydroxyalkane sulfonates or mixtures of alkene sulfonates and hydroxyalkane sulfonates. These olefin sulfonate detergents may be prepared in a known manner by the reaction of sulfur trioxide (SO_3) with long-chain olefins containing 8 to 25, preferably 12 to 21 carbon atoms and having the formula $RCH=CHR_1$ where R is a higher alkyl group of 6 to 23 carbons and R_1 is an alkyl group of 1 to 17 carbons or hydrogen to form a mixture of sultones and alkene sulfonic acids which is then treated to convert the sultones to sulfonates. Preferred olefin sulfonates contain from 14 to 16 carbon atoms in the R alkyl group and are obtained by sulfonating an alpha-olefin.

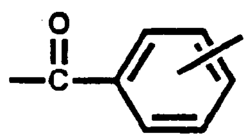
Other examples of suitable anionic sulfonate surfactants are the paraffin sulfonates containing about 10 to 20, preferably about 13 to 17, carbon atoms. Primary paraffin sulfonates are made by reacting long-chain alpha olefins and bisulfites and paraffin sulfonates having the sulfonate group distributed along the paraffin chain are shown in U.S. Patents Nos.. 2,503,280; 2,507,088; 3,260,744; 3,372,188; and German Patent 735,096.

Examples of satisfactory anionic sulfate surfactants are the C_8-C_{18} alkyl sulfate salts and the C_8-C_{18} alkyl ether polyethenoxy sulfate salts having the formula $R(OC_2H_4)n\ OSO_3M$ wherein n is 1 to 12, preferably 1 to 5, and M is a solubilizing cation selected from the group consisting of sodium, potassium, ammonium, magnesium and mono-, di- and triethanol ammonium ions. The alkyl sulfates may be obtained by sulfating the alcohols obtained by reducing glycerides of coconut oil or tallow or mixtures thereof and neutralizing the resultant product.

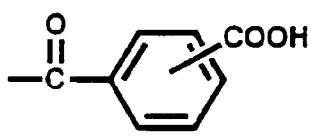
The alkyl sulfates may be obtained by sulfating the alcohols obtained by reducing glycerides of coconut oil or tallow or mixtures thereof and neutralizing the resultant product. On the other hand, the alkyl ether polyethenoxy sulfates are obtained by sulfating the condensation product of ethylene oxide with a C_8-C_{18} alkanol and neutralizing the resultant product. The alkyl ether polyethenoxy sulfates differ from one another in the number of moles of ethylene oxide reacted with one mole of alkanol. Preferred alkyl sulfates and preferred alkyl ether polyethenoxy sulfates contain 10 to 16 carbon atoms in the alkyl group.

The C_8-C_{12} alkylphenyl ether polyethenoxy sulfates containing from 2 to 6 moles of ethylene oxide in the molecule also are suitable for use in the inventive compositions. These surfactants can be prepared by reacting an alkyl phenol with 2 to 6 moles of ethylene oxide and sulfating and neutralizing the resultant ethoxylated alkylphenol.

Other suitable anionic surfactants are the C_9-C_{15} alkyl ether polyethenoxyl carboxylates having the structural formula $R(OC_2H_4)_nOX\ COOH$ wherein n is a number from 4 to 12, preferably 5 to 10 and X is selected from the group consisting of CH_2, $C(O)R_1$ and



wherein R_1 is a C_1-C_3 alkylene group. Preferred compounds include C_9-C_{11} alkyl ether polyethenoxy (7-9) C(O) CH_2CH_2COOH, C_{13}-C_{15} alkyl ether polyethenoxy (7-9)



and C_{10}-C_{12} alkyl ether polyethenoxy (5-7) CH_2COOH. These compounds may be prepared by condensing ethylene oxide with appropriate alkanol and reacting this reaction product with chloracetic acid to make the ether carboxylic acids as shown in U.S. Pat. No. 3,741,911 or with succinic anhydride or phthalic anhydride.

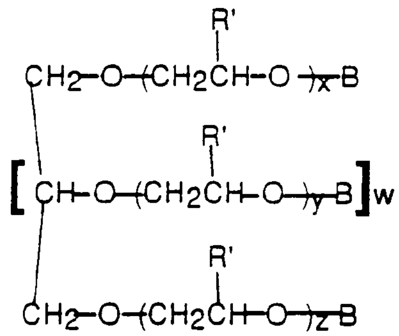
Obviously, these anionic surfactants will be present either in acid form or salt form depending upon the pH of the final composition, with the salt forming cation being the same as for the other anionic detergents.

The preferred anionic surfactants present in the o/w microemulsions are selected from the group consisting of alkali metal salts of an alkyl sulfate surfactant, alkaline earth metal salts of an alkyl sulfate and alkali metal salts of a dialkyl sulfosuccinic acid and mixtures thereof.

Generally, the proportion of the nonsoap-anionic surfactant will be in the range of 0% to 6.0%, preferably from 0.1% to 5%, by weight of the dilute o/w microemulsion composition.

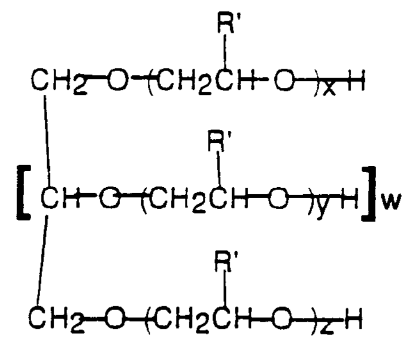
The instant compositions can contain about 0% to about 8% by weight, more preferably 0.25% to about 7% by weight of an alkali metal dialkyl sulfosuccinate surfactant, wherein the dialkyl groups can be the same or different and each dialkyl group has about 4 to about 12 carbon atoms, more preferably about 7 to about 9 carbon atoms and the alkali metal is selected from the group consisting of sodium, potassium and lithium. The preferred alkali metal dialkyl sulfosuccinate of the instant invention is sodium dioctyl sulfosuccinate.

The instant composition contains a composition (herein after referred to as ethoxylated glycerol type compound) which is a mixture of a fully esterified ethoxylated polyhydric alcohol, a partially esterified ethoxylated polyhydric alcohol and a nonesterified ethoxylated polyhydric alcohol, wherein the preferred polyhydric alcohol is glycerol, and the compound is a mixture of



Formula (I)

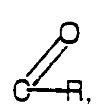
and



Formula (II)

wherein w equals one to four, most preferably one. B is selected from the group consisting of hydrogen or a group represented by:

wherein R is selected from the group consisting of alkyl group having about 6 to 22 carbon atoms, more preferably about 11 to about 15 carbon atoms and alkenyl groups having about 6 to 22 carbon atoms, more preferably about 11 to 15 carbon atoms, wherein a hydrogenated tallow alkyl chain or a coco alkyl chain is most preferred, wherein at least one of the B groups is represented by said



and R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, more preferably 0 to 40, provided that (x+y+z) equals about 2 to about 100, preferably 4 to about 24 and most preferably about 4 to 19, wherein in Formula (I) the ratio of monoester / diester / triester is 45 to 90 / 5 to 40 / 1 to 20, more preferably 50 to 90 / 9 to 32 / 1 to 12, wherein the ratio of Formula (I) to Formula (II) is a value between about 3 to about 0.02, preferably 3 to about 0.1, most preferably about 1.5 to about 0.2, wherein it is most preferred that there is more of Formula (II) than Formula (I) in the mixture that forms the compound.

The ethoxylated glycerol type compound used in the instant composition is manufactured by the Kao Corporation and sold under the trade name Levenol such as Levenol F-200 which has an average EO of 6 and a molar ratio of coco fatty acid to glycerol of 0.55 or Levenol V501/2 which has an average EO of 17 and a molar ratio of tallow fatty acid to glycerol of 1.0. It is preferred that the molar ratio of the fatty acid to glycerol is less than about 1.7, more preferably less than about 1.5 and most preferably less than about 1.0. The ethoxylated glycerol type compound has a molecular weight of about 400 to about 1600, and a pH (50 grams / liter of water) of about 5-7. The Levenol compounds are substantially non irritant to human skin and have a primary biodegradabillity higher than 90% as measured by the Wickbold method Bias-7d.

Two examples of the Levenol compounds are Levenol V-501/2 which has 17 ethoxylated groups and is derived from tallow fatty acid with a fatty acid to glycerol ratio of 1.0 and a molecular weight of about 1465 and Levenol F-200 has 6 ethoxylated groups and is derived from coco fatty acid with a fatty acid to glycerol ratio of 0.55. Both Levenol F-200 and Levenol V-501/2 are composed of a mixture of Formula (I) and Formula (II). The Levenol compounds has ecoxicity values of algae growth inhibition > 100 mg/liter; acute toxicity for Daphniae > 100 mg/liter and acute fish toxicity > 100 mg/liter. The Levenol compounds have a ready biodegradability higher than 60% which is the minimum required value according to OECD 301B measurement to be acceptably biodegradable.

Polyesterified nonionic compounds also useful in the instant compositions are Crovol PK-40 and Crovol PK-70 manufactured by Croda GMBH of the Netherlands. Crovol PK-40 is a polyoxyethylene (12) Palm Kernel Glyceride which has 12 EO groups. Crovol PK-70 which is prefered is a polyoxyethylene (45) Palm Kernel Glyceride have 45 EO groups.

In the dilute o/w microemulsion compositions or liquid crystal compositions the ethoxylated glycerol type compounds or the polyesterified nonionic compounds will be present in admixture with the anionic detergent. The proportion of the ethoxylated glycerol type compound or the polyesterified nonionic solubilizing agent based upon the weight of the liquid crystal composition or the final dilute o/w microemulsion composition will be 0.1% to 20%, more preferably 0.5% to 10%, most preferably about 0.5% to 6% by weight.

Other polyesterfied nonionic surfactants useful in the instant compositions are Crovol PK-40 and Crovol PK-70 manufactured by Croda GMBH of the Netherlands. Crovol PK40 is a polyoxyethylene (12) Palm Kernel Glyceride which has 12 EO groups. Crovol PK70, which is preferred, is a polyoxyethylene (45) Palm Kernel Glyceride have 45 EO groups.

In the preferred dilute o/w microemulsion compositions the esterfied ethoxylated glycerol type compound will be present in admixture with the anionic surfactant. The proportion of the esterfied ethoxylated glycerol type compound based upon the weight of the final dilute o/w microemulsion composition will be 0.1% to 20.0%, more preferably 0.5% to 10%, by weight.

The cosurfactant may play an essential role in the formation of the dilute o/w microemulsion and the concentrated microemulsion compositions. Very briefly, in the absence of the cosurfactant, the water, detergent(s) and hydrocarbon (e.g., perfume) will, when mixed in appropriate proportions, form either a micellar solution (low concentration) or form an oil-in-water emulsion in the first aspect of the invention. With the cosurfactant added to this system, the interfacial tension at the interface between the emulsion droplets and aqueous phase is reduced to a very low value. This reduction of the interfacial tension results in spontaneous break-up of the emulsion droplets to consecutively smaller aggregates until the state of a transparent colloidal sized emulsion. e.g., a microemulsion, is formed. In the state of a microemulsion, thermodynamic factors come into balance with varying degrees of stability related to the total free energy of the microemulsion. Some of the thermodynamic factors involved in determining the total free energy of the system are (1) particle-particle potential; (2) interfacial tension or free energy (stretching and bending); (3) droplet dispersion entropy; and (4) chemical potential changes upon formation. A thermodynamically stable system is achieved when (1) interfacial tension or free energy is minimized and (2) droplet dispersion entropy is maximized.

Thus, the role of cosurfactant in formation of a stable o/w microemulsion is to (a) decrease interfacial tension (1); and (b) modify the microemulsion structure and increase the number of possible configurations (2). Also, the cosurfactant will (c) decrease the rigidity at the interfacial layer of the micelle.

Generally, an increase in cosurfactant concentration results in a wider temperature range of the stability of the product.

Three major classes of compounds have been found to provide highly suitable cosurfactants over temperature ranges extending from 5°C to 43°C for instance; (1) water-soluble C_3-C_5 alkanols, polypropylene glycol of the formula $HO(CH_3CHCH_2O)_nH$ wherein n is a number from 2 to 18 and mono C_1-C_6 alkyl ethers and esters of ethylene glycol and propylene glycol having the structural formulas $R(X)_nOH$ and $R_1(X)_nOH$ wherein R is C_1-C_6 alkyl, R_1 is C_2-C_4 acyl group, X is (OCH_2CH_2) or (OCH_2CH_3CH) and n is a number from 1 to 4; (2) aliphatic mono- and di-carboxylic acids containing 2 to 10 carbon atoms, preferably 3 to 6 carbons in the molecule; and (3) triethyl phosphate. Additionally, mixtures of two or more of the three classes of cosurfactant compounds may be employed where specific pH's are desired.

When the mono- and di-carboxylic acid (Class 2) cosurfactants are employed in the instant microemulsion compositions at a concentration of about 2 to 10 wt. %, the microemulsion compositions can be used as cleaners for bathtubs and other hard surfaced items, which are acid resistant thereby removing lime scale, soap scum and greasy soil from the surfaces of such items damaging such surfaces. If these surfaces are of zirconium white enamel, they can be damaged by these compositions.

An aminoalkylene phosphonic acid at a concentration of about 0.01 to about 0.2 wt. % can be optionally used in conjunction with the mono- and di-carboxylic acids, wherein the aminoalkylene phosphonic acid helps prevent damage to zirconium white enamel surfaces. Additionally, 0.05 to 1% of phosphoric acid can be used in the composition.

Representative members of the polypropylene glycol include dipropylene glycol and polypropylene glycol having a molecular weight of 200 to 1000, e.g., polypropylene glycol 400. Other satisfactory glycol ethers are ethylene glycol monobutyl ether (available as Butyl Cellosolve from Union Carbide), diethylene glycol monobutyl ether (Butyl Carbitol), ethylene glycol monohexyl ether (Hexyl Cellosolve), diethylene glycol monohexyl ether (Hexyl Carbitol), triethylene glycol monobutyl ether, mono, di, tri propylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, propylene glycol tertiary butyl ether, ethylene glycol monoacetate and dipropylene glycol propionate.

Representative members of the aliphatic carboxylic acids include C_3-C_6 alkyl and alkenyl monobasic acids and dibasic acids such as glutaric acid and mixtures of glutaric acid with adipic acid and succinic acid, as well as mixtures of the foregoing acids.

While all of the aforementioned glycol ether compounds and acid compounds provide the described stability, the most preferred cosurfactant compounds of each type, on the basis of cost and cosmetic appearance (particularly odor), are diethylene glycol monobutyl ether or diethylene glycol monohexyl ether and a mixture of adipic, glutaric and succinic acids, respectively. The ratio of acids in the foregoing mixture is not particularly critical and can be modified to provide the desired odor. Generally, to maximize water solubility of the acid mixture glutaric acid, the most water-soluble of these three saturated aliphatic dibasic acids, will be used as the major component.

Generally, weight ratios of adipic acid: glutaric acid:succinic acid is 1-3:1-8:1-5, preferably 1-2:1-6:1-3, such as 1:1:1, 1:2:1, 2:2:1, 1:2:1.5, 1:2:2, 2:3:2, etc. can be used with equally good results.

The amount of cosurfactant required to stabilize the microemulsion compositions will, of course, depend on such factors as the surface tension characteristics of the cosurfactant, the type and amounts of the primary surfactants and perfumes, and the type and amounts of any other additional ingredients which may be present in the composition and which have an influence on the thermodynamic factors enumerated above. Generally, amounts of cosurfactant in the range of from 0.1% to 50%, preferably from about 0.5% to 15%, especially preferably from about 1% to 7%, by weight provide stable dilute o/w microemulsions for the above-described levels of primary surfactants and perfume and any other additional ingredients as described below.

As will be appreciated by the practitioner, the pH of the final microemulsion will be dependent upon the identity of the cosurfactant compound, with the choice of the cosurfactant being dependent on cost and cosmetic properties, particularly odor. For example, microemulsion compositions which have a pH in the range of 1 to 10 may employ either the class 1 or the class 3 cosurfactant as the sole cosurfactant, but the pH range is reduced to 1 to 8.5 when the polyvalent metal salt is present. On the other hand, the class 2 cosurfactant can only be used as the sole cosurfactant where the product pH is below 3.2. However, where the acidic cosurfactants are employed in admixture with a glycol ether cosurfactant, compositions can be formulated at a substantially neutral pH (e.g., pH 7±1.5, preferably 7±0.2).

The ability to formulate neutral and acidic products without builders which have grease removal capacities is a feature of the present invention because the prior art o/w microemulsion formulations most usually are highly alkaline or highly built or both.

In addition to their excellent capacity for cleaning greasy and oily soils, the low pH o/w microemulsion formulations also exhibit excellent cleaning performance and removal of soap scum and lime scale in neat (undiluted) as well as in diluted usage.

The final essential ingredient in the inventive microemulsion compositions having improved interfacial tension properties is water. The proportion of water in the microemulsion compositions generally provides the balance of the compositions and may be in the range of 20% to 97%, preferably 70% to 97% by weight of the usual diluted o/w microemulsion composition.

As believed to have been made clear from the foregoing description, the dilute o/w microemulsion liquid all-purpose cleaning compositions of this invention are especially effective when used as is, that is, without further dilution in water, since the properties of the composition as an o/w microemulsion are best manifested in the neat (undiluted) form. However, at the same time it should be understood that depending on the levels of surfactants, cosurfactants, perfume and other ingredients, some degree of dilution without disrupting the microemulsion, per se, is possible. For example, at the preferred low levels of active surfactant compounds (i.e., primary anionic and nonionic detergents) dilutions up to about 50% will generally be well tolerated without causing phase separation, that is, the microemulsion state will be maintained.

However, even when diluted to a great extent, such as a 2- to 10-fold or more dilution, for example, the resulting compositions are still effective in cleaning greasy, oily and other types of soil. Furthermore, the presence of magnesium ions or other polyvalent ions, e.g., aluminum, as will be described in greater detail below further serves to boost cleaning performance of the primary detergents in dilute usage.

On the other hand, it is also within the scope of this invention to formulate highly concentrated microemulsions which will be diluted with additional water before use.

The present invention also relates to a stable concentrated microemulsion or acidic microemulsion composition comprising approximately by weight:

(a) 0% to 6% of an anionic surfactant;
(b) 0.1% to 20% of a mixture of a fully esterfied ethoxylated polyhydric alcohol, a partially esterified ethoxylated polyhydric alcohol and a nonesterified ethoxylated polyhydric alcohol;
(c) 0.1% to 50% of a cosurfactant;
(d) 0.4% to 10% of a water insoluble hydrocarbon or perfume;
(e) 0% to 18% of at least one mono- or dicarboxylic acid;
(f) 0% to 1% of phosphoric acid;
(g) 0% to 0.2% of an aminoalkylene phosphoric acid;
(h) 0% to 15% of magnesium sulfate heptahydrate;
(i) 0% to 16% of a nonionic surfactant;
(j) 0% to 8% of an alkali metal dialkyl sulfosuccinate; and
(k) the balance being water.

Such concentrated microemulsions can be diluted by mixing with up to about 20 times or more, preferably about 4 to about 10 times their weight of water to form o/w microemulsions similar to the diluted microemulsion compositions described above. While the degree of dilution is suitably chosen to yield an o/w microemulsion composition after dilution, it should be recognized that during the course of dilution both microemulsion and non-microemulsions may be successively encountered.

In addition to the above-described essential ingredients required for the formation of the microemulsion composition, the compositions of this invention may often and preferably do contain one or more additional ingredients which serve to improve overall product performance.

One such ingredient is an inorganic or organic salt or oxide of a multivalent metal cation, particularly Mg^{++}. The metal salt or oxide provides several benefits including improved cleaning performance in dilute usage, particularly in soft water areas, and minimized amounts of perfume required to obtain the microemulsion state. Magnesium sulfate, either anhydrous or hydrated (e.g., heptahydrate), is especially preferred as the magnesium salt. Good results also have been obtained with magnesium oxide, magnesium chloride, magnesium acetate, magnesium propionate and magnesium hydroxide. These magnesium salts can be used with formulations at neutral or acidic pH since magnesium hydroxide will not precipitate at these pH levels.

Although magnesium is the preferred multivalent metal from which the salts (inclusive of the oxide and hydroxide) are formed, other polyvalent metal ions also can be used provided that their salts are nontoxic and are soluble in the aqueous phase of the system at the desired pH level.

Thus, depending on such factors as the pH of the system, the nature of the primary surfactants and cosurfactant, and so on, as well as the availability and cost factors, other suitable polyvalent metal ions include aluminum, copper, nickel, iron, calcium, etc. It should be noted, for example, that with the preferred paraffin sulfonate or alkyl sulfate anionic detergents, calcium salts will precipitate and should not be used. It has also been found that the aluminum salts work best at pH below 5 or when a low level, for example about 1 weight percent, of citric acid is added to the composition which is designed to have a neutral pH. Alternatively, the aluminum salt can be directly added as the citrate in such case. As the salt, the same general classes of anions as mentioned for the magnesium salts can be used, such as halide (e.g., bromide, chloride), sulfate, nitrate, hydroxide, oxide, acetate, propionate, etc.

Preferably, in the dilute compositions the metal compound is added to the composition in an amount sufficient to provide at least a stoichiometric equivalent between the anionic surfactant and the multivalent metal cation. For example, for each gram-ion of Mg++ there will be 2 gram moles of paraffin sulfonate, alkylbenzene sulfonate, alkyl sulfate, etc., while for each gram-ion of Al^{3+} there will be 3 gram moles of anionic surfactant. Thus, the proportion of the multivalent salt generally will be selected so that one equivalent of compound will neutralize from 0.1 to 1.5 equivalents, preferably 0.9 to 1.4 equivalents, of the acid form of the anionic detergent. At higher concentrations of anionic detergent, the amount of multivalent salt will be in range of 0.5 to 1 equivalents per equivalent of anionic detergent.

The o/w microemulsion compositions can include from 0% to 2.5%, preferably from 0.1% to 2.0% by weight of the composition of a C_8-C_{22} fatty acid or fatty acid soap as a foam suppressant.

The addition of fatty acid or fatty acid soap provides an improvement in the rinseability of the composition whether applied in neat or diluted form. Generally, however, it is necessary to increase the level of cosurfactant to maintain product stability when the fatty acid or soap is present.

As example of the fatty acids which can be used as such or in the form of soap, mention can be made of distilled coconut oil fatty acids, "mixed vegetable" type fatty acids (e.g. high percent of saturated, mono-and/or polyunsaturated C_{18} chains); oleic acid, stearic acid, palmitic acid, eiocosanoic acid, and the like, generally those fatty acids having from 8 to 22 carbon atoms being acceptable.

The all-purpose liquid cleaning composition of this invention may, if desired, also contain other components either to provide additional effect or to make the product more attractive to the consumer. The following are mentioned by way of example: Colors or dyes in amounts up to 0.5% by weight; bactericides in amounts up to 1% by weight; preservatives or antioxidizing agents, such as formalin, 5-chloro-2-methyl-4-isothaliazolin-3-one; 2,6-di-tert-butyl-p-cresol, etc., in amounts up to 2% by weight; and pH adjusting agents, such as sulfuric acid or sodium hydroxide, as needed. Furthermore, if opaque compositions are desired, up to 4% by weight of an opacifier may be added.

The instant compositions do not contain any alkali metal silicates or alkali metal detergent builder salts such as alkali metal phosphonates, alkali metal carbonates, alkali metal polyphosphates or alkali metal citrates because, if these materials are used in the instant composition, they will make the compositions too caustic and leave a residue on the surface being cleaned. The instant compositions do not contain any betaine surfactants because, if betaine surfactants are used in the instant composition, the foam profile of the instant compositions would be too high. The concentration of the fatty acid used in the instant compositions must be less than 2.5 wt. % because at concentrations higher than 2.5 wt. % of the fatty acid, the composition would have an objectionable smell as well. The instant-compositions do not contain any methanol or ethanol because of their extremely low flash points.

In final form, the all-purpose liquids are clear oil-in-water microemulsions and exhibit stability at reduced and increased temperatures. More specifically, such compositions remain clear and stable in the range of 5°C to 50°C, especially 10°C to 43°C. Such compositions exhibit a pH in the acid or neutral range depending on intended end use. The liquids are readily pourable and exhibit a viscosity in the range of 6 to 60 milliPascal · second (mPas) as measured at 25°C with a Brookfield RVT Viscometer using a #1 spindle rotating at 20 RPM. Preferably, the viscosity is maintained in the range of 10 to 40 mPas.

The compositions are directly ready for use or can be diluted as desired and in either case no or only minimal rinsing is required and substantially no residue or streaks are left behind. Furthermore, because the compositions are free of detergent builders such as alkali metal polyphosphates they are environmentally acceptable and provide a better "shine" on cleaned hard surfaces.

When intended for use in the neat form, the liquid compositions can be packaged under pressure in an aerosol container or in a pump or trigger-type sprayer for the so-called spray-and-wipe type of application.

Because the compositions as prepared are aqueous liquid formulations and since no particular mixing is required to form the o/w microemulsion, the compositions are easily prepared simply by combining all the ingredients in a suitable vessel or container. The order of mixing the ingredients is not particularly important and generally the various ingredients can be added sequentially or all at once or in the form of aqueous solutions of each or all of the primary detergents and cosurfactants can be separately prepared and combined with each other and with the perfume. The magnesium salt, or other multivalent metal compound, when present, can be added as an aqueous solution thereof or can be added directly. It is not necessary to use elevated temperatures in the formation step and room temperature is sufficient.

It is contemplated within the scope of the instant invention that the instant esterified ethoxylated glycerol type compounds can be employed in hard surface cleaning compositions such as wood cleaners, window cleaners and light duty liquid cleaners as a total or partial replacement for the anionic and/or nonionic surfactants of these hard surface cleaning compositions, wherein improvements in a grease release effect is desirable.

The following examples illustrate liquid cleaning compositions of the described invention. The exemplified compositions are illustrative only and do not limit the scope of the invention. Unless otherwise specified, the proportions in the examples and elsewhere in the specification are by weight.

Example 1

The following compositions in wt. % were prepared:

	A	B	C	D	Ajax Frais
Magnesium Lauryl sulfate	0.1				
Nonionic surfactant - Neodol 45-7	2.0		1.2		
Esterfied polyethoxyether nonionic Levenol F200 surfactant	4.0	4.5	3.6	4.5	
Sodium Dioctyl sulfosuccinate		1.5		1.5	
Diethylene glycol monohexyl ether	3	3	3	4	
Tallow PKO soap			0.2	0.15	
MgSO4 7 H2O		0.25	0.5	0.25	
Nicky LCV Perfume(a)	0.8	0.8	0.8	0.8	
Na Lauryl Sulfate			1.2		
Dodecane			0.2	0.15	
Water + Minors	Bal	Bal	Bal	Bal.	
pH	7	7	7	7	
Grease cleaning test Neat (b) 10 strokes Dilute (b) 50 strokes	 80 50	 100 40	 40 35	 100 40	 100 35

(a) contains about 25% by weight of terpenes.

(b) the higher the percent cleaning, the better the degreasing performance.

The Grease Cleaning Performance Test was performed as follows:

15 cm x 15 cm white Formica tiles were washed with soap and warm water then rinsed with water, deionized water and finally ethanol and then dried at room temperature for at least 4 hours. Tiles were used once then discarded. The tiles were then sprayed with a chloroform solution of dye and grease using a laboratory chromatography sprayer. In-house compressed air at a pressure of approximately 30 PSI was used for spraying. The following ratios were used to prepare the solution for spraying; Neat, 5% hard tallow, 5% soft tallow, 0.01% D&C red 17 in Chloroform; Dilute, 1.0% hard tallow, 1.0% soft tallow, 0.01% D&C red 17. To aid in preparation of the soil, a stock solution of 1% dye in chloroform was prepared so that 1.0 g of this solution in 100 g would give the correct final dye concentration. The tiles were sprayed such that the reflectance (Rd) of the soiled tile was between 63-70. The tiles were used 15 minutes after spraying to allow the chloroform to evaporate.

The soiled tile was placed in a Gardner Abrader fitted with a two path/two boat sled. Compressed sponges were inserted into the two boats. Each boat was filled with 300 g of lead shot to ensure that the same force is applied to each sponge.

For testing dilute cleaning, 1.2% solutions of two formulas were prepared and approximately 50 mls of each solution were placed in separate 14 cm x 7 cm Pyrex dishes. A boat fitted with a compressed sponge was placed in each solution. The solutions were allowed to saturate the sponges for 1-2 minutes and the excess was removed by rubbing the sponge across the side of the dish. The boats were then placed in the abrader sled and it was operated for 15 strokes. The boats were removed and the sponges were squeezed dry against the side of a sink and were resaturated with fresh solution from the dishes. The excess was removed and the abrader process was repeated. This process was repeated every 15 strokes for a total of 105 strokes. The Rd values of the tiles were read before and after soiling and after every 15 strokes using a Photovolt model 575 reflectometer. The Rd values were read without removing the tiles from the abrader. Three areas on each cleaned portion were read and averaged.

For testing neat cleaning, two boats were fitted with compressed sponge and placed in separate 14 cm x 7 cm Pyrex dishes filled with approximately 50 ml tap water. The sponges were allowed to saturate with the water and the excess was removed by rubbing the sponge against the side of the dish. On each sponge was placed 1.0 ml of one of the two cleaning formulations. The boats were placed in the abrader and it was operated for 1, 3, 5, 10, 20, 35, and 50 strokes, stopping between to measure the Rd value. Again, the readings were made without removing the tile from the abrader. Three areas on each cleaned portion were read and averaged. The solutions were not replenished during the test.

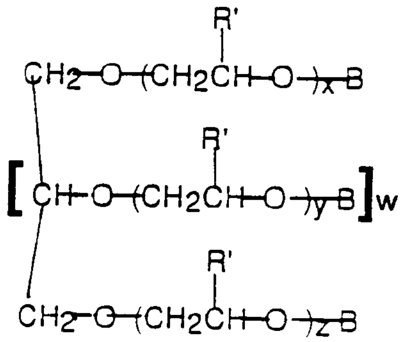
The % cleaning was calculated according to the following equation:

$$\%\ \text{Cleaned} = \frac{\text{Reflectance of cleaned tile} - \text{reflectance of soiled tile}}{\text{reflectance of unsoiled tile} - \text{reflectance of soiled tile}}\ 100$$

In summary, the described invention broadly relates to an improvement in microemulsion compositions containing an anionic surfactant, an esterified ethoxylated glycerol type compound, one of the specified co-surfactants, a hydrocarbon ingredient and water which comprise the use of a water-insoluble, odoriferous perfume as the essential hydrocarbon ingredient in a proportion sufficient to form either a dilute o/w microemulsion composition containing, by weight, 0.1% to 6.0% of an anionic detergent, 0 to 16% of a nonionic surfactant, 0.1% to 20% an esterfied ethoxylated glycerol type compound, 0.1% to 50% of cosurfactant, 0.4% to 10% of perfume or hydrocarbon and the balance being water.

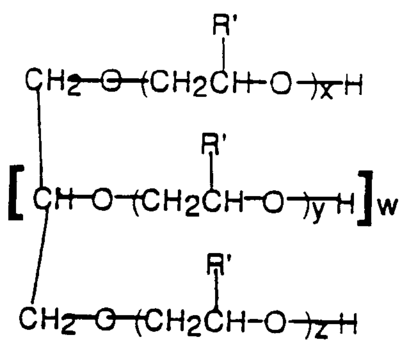
Claims

1. A stable microemulsion composition comprising approximately by weight: 0.1% to 6% of an anionic surfactant 0 to 16% of a nonionic surfactant, 0.1% to 50% of a cosurfactant, 0.1% to 20% of a mixture of



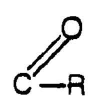
(I)

and

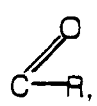


(II)

wherein w equals one to four, B is selected from the group consisting of hydrogen or a group represented by:

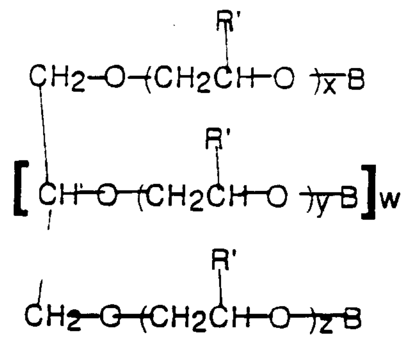


wherein R is selected from the group consisting of alkyl group having about 6 to 22 carbon atoms, and alkenyl groups having about 6 to 22 carbon atoms, wherein at least one of the B groups is represented by said



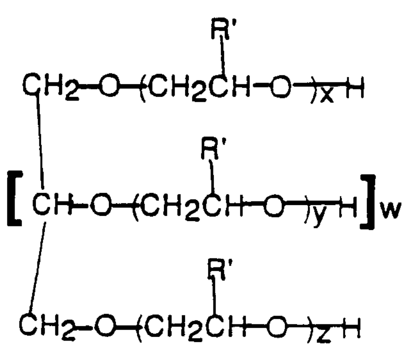
R' is selected from the group consisting of hydrogen and methyl groups: x, y and z have a value between 0 and 60, provided that (x+y+z) equals about 2 to about 100, wherein in Formula (I) the ratio of monoester / diester / triester is 40 to 90 / 5 to 35 / 1 to 20, wherein the ratio of Formula (I) to Formula (II) is a value between about 3 to about 0.02, 0.4% to 10% of at least one water insoluble hydrocarbon and/or a perfume and the balance being water.

2. A stable, clear, all-purpose, hard surface cleaning composition which is especially effective in the removal of oily and greasy soil being in the form of an oil-in-water microemulsion (o/w), the aqueous phase of said microemulsion composition comprising approximately by weight: from about 0.1% to 6% of an anionic surfactant; 0 to 16% of a nonionic surfactant; 0.1% to 20% of a mixture of



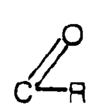
(I)

and

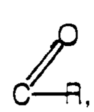


(II)

wherein w equals one to four. B is selected from the group consisting of hydrogen or a group represented by:



wherein R is selected from the group consisting of alkyl group having about 6 to 22 carbon atoms, and alkenyl groups having about 6 to 22 carbon atoms, wherein at least one of the B groups is represented by said

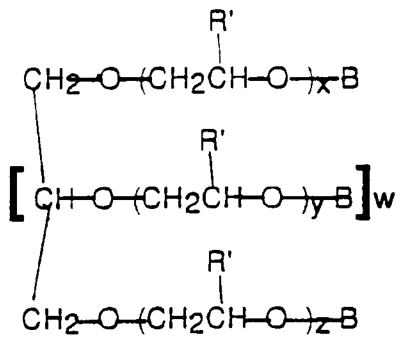


R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, provided that (x+y+z) equals about 2 to about 100, wherein in Formula (I) the ratio of monoester / diester / triester is 40 to 90 / 5 to 35 / 1 to 20, wherein the ratio of Formula (I) to Formula (II) is a value between about 3 to about 0.02, from about 0.1% to about 50% of a cosurfactant having substantially no ability to dissolve oily or greasy soil selected from the group consisting of C_3-C_5 alkanols, polypropylene glycol and C_1-C_6 alkyl ethers and esters of ethylene glycol or propylene glycol, aliphatic mono- and dicarboxylic acids containing 3 to 6 carbons in the molecule, and mono-, di- and triethyl phosphate and water; the oil phase of said microemulsion consisting essentially of at least one water-immiscible or hardly water-soluble hydrocarbon ingredient in an amount of from about 0.1% to about 10% by weight of the entire composition, said composition being particularly effective in removing oily or greasy soil from hard surfaces by solubilizing the oily or greasy soil in the oil phase of said microemulsion.

3. A stable concentrated microemulsion composition comprising approximately by weight:

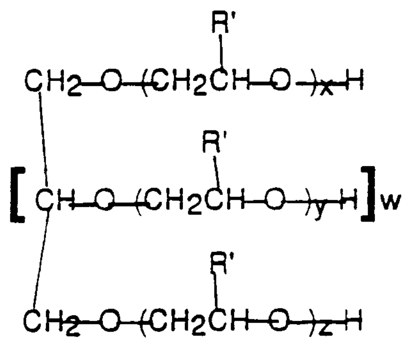
(a) 1 to 30% of an anionic surfactant;

(b) 0.1% to 20% of a mixture of



(I)

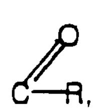
and



(II)

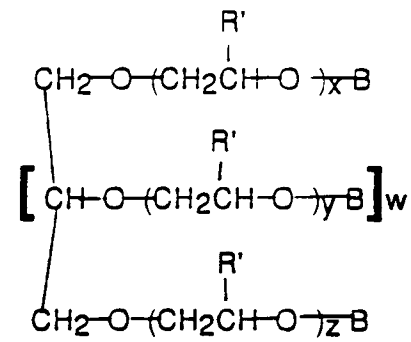
wherein w equals one to four, B is selected from the group consisting of hydrogen or a group represented by:

wherein R is selected from the group consisting of alkyl group having about 6 to 22 carbon atoms, and alkenyl groups having about 6 to 22 carbon atoms, wherein at least one of the B groups is represented by said



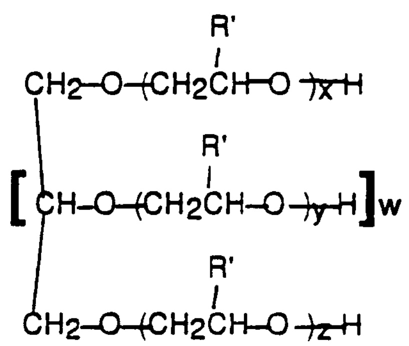
R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, provided that (x+y+z) equals about 2 to about 100, wherein in Formula (I) the ratio of monoester / diester / triester is 40 to 90 / 5 to 35 / 1 to 20, wherein the ratio of Formula (I) to Formula (II) is a value between about 3 to about 0.02,
(c) 0.1% to 50% of a cosurfactant;
(d) 0.4 to 10% of at least one water insoluble hydrocarbon or perfume;
(e) 0 to 18% of at least one mono- or dicarboxylic acid;
(f) 0 to 0.2% of an aminoalkylene phosphonic acid;
(g) 0 to 1.0% of phosphoric acid;
(h) 0 to 15% of magnesium sulfate heptahydrate;
(i) 0 to 16% of a nonionic surfactant; and
(j) the balance being water.

4. A stable microemulsion composition comprising approximately by weight: 0.25% to 8% of an alkali metal dialkyl sulfosuccinate, 0.1% to 50% of a cosurfactant, 0.1% to 20% of a mixture of



(I)

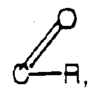
and



(II)

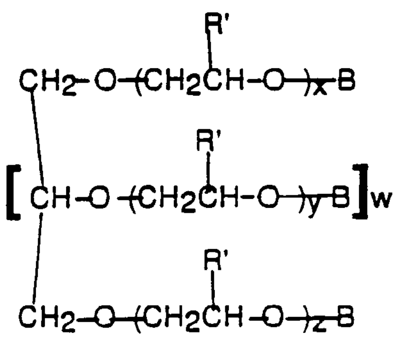
wherein w equals one to four, B is selected from the group consisting of hydrogen or a group represented by:

wherein R is selected from the group consisting of alkyl group having about 6 to 22 carbon atoms, and alkenyl groups having about 6 to 22 carbon atoms, wherein at least one of the B groups is represented by said



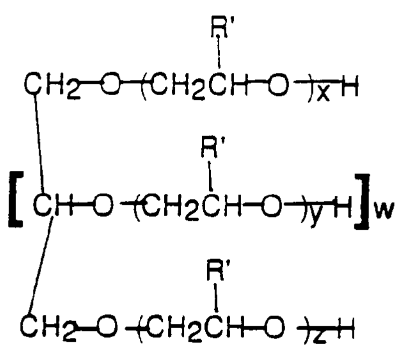
R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, provided that (x+y+z) equals about 2 to about 100, wherein in Formula (I) the ratio of monoester / diester / triester is 40 to 90 / 5 to 35 / 1 to 20, wherein the ratio of Formula (I) to Formula (II) is a value between about 3 to about 0.02, 0.4% to 10% of at least one water insoluble hydrocarbon and/or a perfume and the balance being water.

5. A stable, clear, all-purpose, hard surface cleaning composition which is especially effective in the removal of oily and greasy soil being in the form of an oil-in-water microemulsion (o/w), the aqueous phase of said microemulsion composition comprising approximately by weight from about 0.25% to 8% of an alkali metal dialkyl sulfosuccinate, 0.1% to 20% of a mixture of



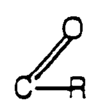
(I)

and

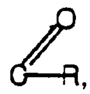


(II)

wherein w equals one to four, B is selected from the group consisting of hydrogen or a group represented by:

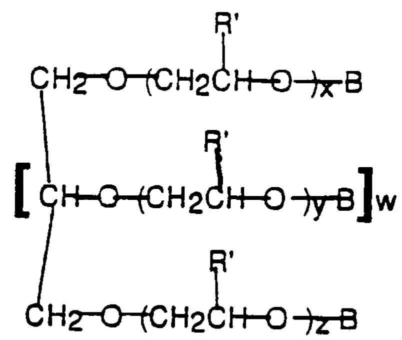


wherein R is selected from the group consisting of alkyl group having about 6 to 22 carbon atoms, and alkenyl groups having about 6 to 22 carbon atoms, wherein at least one of the B groups is represented by said



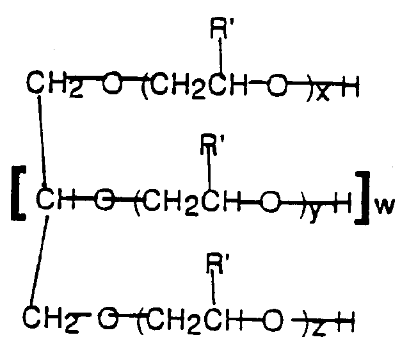
R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, provided that (x+y+z) equals about 2 to about 100, wherein in Formula (I) the ratio of monoester / diester / triester is 40 to 90 / 5 to 35 / 1 to 20, wherein the ratio of Formula (I) to Formula (II) is a value between about 3 to about 0.02, from about 0.1% to about 50% of a water-miscible cosurfactant having substantially no ability to dissolve oily or greasy soil selected from the group consisting of C_3-C_5 alkanols, polypropylene glycol and C_1-C_6 alkyl ethers and esters of ethylene glycol or propylene glycol, aliphatic mono- and di- carboxylic acids containing 3 to 6 carbons in the molecule, and mono-, di- and triethyl phosphate and water; the oil phase of said microemulsion consisting essentially of at least one water-immiscible or hardly water-soluble hydrocarbon ingredient in an amount of from about 0.1% to about 10% by weight of the entire composition, said composition being particularly effective in removing oily or greasy soil from hard surfaces by solubilizing the oily or greasy soil in the oil phase of said microemulsion.

6. A stable concentrated microemulsion composition comprising approximately by weight:
(a) 0.1% to 20% of a mixture of



(I)

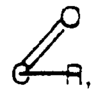
and



(II)

wherein w equals one to four, B is selected from the group consisting of hydrogen or a group represented by:

wherein R is selected from the group consisting of alkyl group having about 6 to 22 carbon atoms, and alkenyl groups having about 6 to 22 carbon atoms, wherein at least one of the B groups is represented by said



R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, provided that (x+y+z) equals about 2 to about 100, wherein in Formula (I) the ratio of monoester / diester / triester is 40 to 90 / 5 to 35 / 1 to 20, wherein the ratio of Formula (I) to Formula (II) is a value between about 3 to about 0.02,
(b) 0.1% to 50% of a cosurfactant;
(c) 0.4 to 10% of at least one water insoluble hydrocarbon or perfume;
(d) 0 to 18% of at least one mono- or dicarboxylic acid;
(e) 0 to 0.2% of an aminoalkylene phosphonic acid;
(f) 0 to 1.0% of phosphoric acid;
(g) 0 to 15% of magnesium sulfate heptahydrate;
(h) 0.25% to 8% of an alkali metal dialkyl sulfosuccinate, wherein each of said alkyl groups have about 4 to about 12 carbon atoms and said alkali metal is selected from the group consisting of lithium, potassium and sodium; and
(i) the balance being water.

7. A cleaning composition of anyone of claims 1 to 6 characterised in that it further contains a multivalent metal cation in an amount sufficient to provide from 0.5 to 1.5 equivalents of said cation per equivalent of said anionic detergent.

8. A cleaning composition of claim 7 characterised in that the multivalent metal cation is magnesium or aluminium.

9. A cleaning composition of claim 7 or claim 8 characterised in that the said composition contains 0.9 to 1.4 equivalents of said cation per equivalent of anionic detergent.

10. A cleaning composition of claim 8 or claim 9 characterised in that the said multivalent salt is magnesium oxide or magnesium sulfate.

11. A cleaning composition of anyone of claims 1 to 10 characterised in that the said fatty acid has about 8 to about 22 carbon atoms.

12. A cleaning composition of anyone of claims 1 to 11 characterised in that it contains from about 0.5 - 15% by weight of said cosurfactant and from 0.4% to about 3.0% by weight of said hydrocarbon.

13. A cleaning composition of anyone of claims 1 to 12 characterised in that the cosurfactant is a glycol ether that has an alkyl chain length of 1 to 6 carbons.

14. A cleaning composition of claim 13 wherein the glycol ether is selected from the group consisting of ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, polypropylene glycol having an average molecular weight of from about 200 to 1,000, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, triethylene glycol monohexyl ether and propylene glycol tert butyl ether, and mono, di, or tri propylene glycol monobutyl ether.

15. A cleaning composition of claim 14 wherein the glycol ether is ethylene glycol monobutyl ether, diethylene glycol monobutyl ether or diethylene glycol monohexyl ether.

16. A cleaning composition of anyone of claims 1 to 15 characterised in that the cosurfactant is a C_3-C_6 aliphatic carboxylic acid selected from the group consisting of adipic acid, propionic acid, glutaric acid, mixtures of glutaric acid and succinic acid and adipic acid and mixtures of any of the foregoing.

17. A cleaning composition of claim 16 characterised in that the aliphatic carboxylic acid is a mixture of adipic acid, glutaric acid and succinic acid.

18. A cleaning composition of anyone of claims 1 to 17 characterised in that the anionic surfactant is a C_9-C_{15} alkyl benzene sulfonate or a C_{10}-C_{20} alkane sulfonate.

19. A cleaning composition of anyone of claims 4, 5 or 6 characterised in that the said alkali metal of said alkali metal dialkyl sulfosuccinate is selected from the group consisting of lithium, potassium and sodium and said alkyl groups each have about 4 to about 12 carbon atoms.