

⑫

EUROPEAN PATENT SPECIFICATION

④ Date of publication of patent specification: **24.02.88**

⑤ Int. Cl.⁴: **C 11 D 3/43, C 11 D 3/18,**
C 11 D 3/20, C 11 D 17/00

⑦ Application number: **83109923.9**

⑧ Date of filing: **20.05.81**

⑨ Publication number of the earlier application in accordance with Art. 76 EPC: **0 040 882**

⑤ **Terpene-solvent mixture useful for making liquid detergent compositions.**

③ Priority: **27.05.80 GB 8017364**

④ Date of publication of application:
25.04.84 Bulletin 84/17

⑤ Publication of the grant of the patent:
24.02.88 Bulletin 88/08

⑧ Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

⑩ References cited:
GB-A-1 237 874
GB-A-1 603 047
GB-A-2 033 421
US-A-3 634 338
US-E- 29 649

Marsden's Solvents Guide; Perry's Chemical Engineers' Handbook

⑦ Proprietor: **THE PROCTER & GAMBLE COMPANY**

301 East Sixth Street
Cincinnati Ohio 45201 (US)

⑧ **CH GB LI SE AT**

⑦ Proprietor: **Procter & Gamble European Technical Center**
Temselaan 100
B-1820 Strombeek-Bever (BE)

⑧ **BE DE FR IT NL**

⑦ Inventor: **Goffinet, Pierre Charles Emile**
Residence Flotte No. 6 Avenue Ferdinand Flotte
F-13008 Marseille (FR)

⑦ Representative: **Brooks, Maxim Courtney et al**
Procter & Gamble (NTC) Limited Whitley Road
Longbenton
Newcastle-upon-Tyne NE12 9TS (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Description

This invention relates to terpene-solvent mixtures useful for making liquid detergent compositions. In particular, it relates to mixtures useful for making aqueous detergent compositions suitable for use as
 5 general purpose household cleaning compositions.

General purpose household cleaning compositions for hard surfaces such as metal, glass, ceramic, plastic and linoleum surfaces, are commercially available in both powdered and liquid form. Powdered cleaning compositions consist mainly of builder or buffering salts such as phosphates, carbonates, silicates etc., and although such compositions may display good inorganic soil removal, they are generally deficient
 10 in cleaning ability on organic soils such as the grease/fatty/oily soils typically found in the domestic environment.

Liquid cleaning compositions, on the other hand, have the great advantage that they can be applied to hard surfaces in neat or concentrated form so that a relatively high level of surfactant material is delivered directly to the soil. Moreover, it is a rather more straightforward task to incorporate high concentrations of
 15 anionic or nonionic surfactant in a liquid rather than a granular composition. For both these reasons, therefore, liquid cleaning compositions have the potential to provide superior grease and oily soil removal over powdered cleaning compositions.

Nevertheless, liquid cleaning compositions still suffer a number of drawbacks which can limit their consumer acceptability. Thus, they generally contain little or no detergency builder salts and consequently
 20 they tend to have poor cleaning performance on particulate soil and also lack "robustness" under varying water hardness levels. In addition, they can suffer problems of product form, in particular, inhomogeneity, lack of clarity, or inadequate viscosity characteristics for consumer use. Moreover, the higher in-product and in-use surfactant concentration necessary for improved grease handling raises problems of extensive suds formation requiring frequent rinsing and wiping on behalf of the consumer. Although oversudsing
 25 may be controlled to some extent by incorporating a suds-regulating material such as hydrophobic silica and/or silicone or soap, this in itself can raise problems of poor product stability and homogeneity and also problems associated with deposition of insoluble particulate or soap residues on the items or surfaces being cleaned, leading to filming, streaking and spotting.

It has now been discovered, however, that these defects of prior art liquid cleaning composition can be
 30 minimized or overcome through the incorporation therein of a specified level of mono- or sesquiterpene material in combination with a selected polar solvent. Although the terpenes, as a class, have limited water-solubility, it has now been found that they can be incorporated into liquid cleaning compositions in homogeneous form, even under "cold" processing conditions, with the ability to provide excellent cleaning characteristics across the range of water hardness on grease/oily soils and inorganic particulate
 35 soils, as well as on shoe polish, marker ink, bath tub soil etc, and excellent shine performance with low soil redeposition and little or no propensity to cause filming, streaking or spotting on surfaces washed therewith. Moreover, the terpenes herein specified, and in particular those of the hydrocarbon class, are valuable in regulating and sudsing behaviour of the instant compositions in both hard and soft water and under both diluted and neat or concentrated usage, while terpenes of the terpene alcohol class are also
 40 valuable for providing effective control of product viscosity characteristics.

Terpenes are, of course, well-known components of perfume compositions and are often incorporated into detergent compositions at low levels via the perfume. Certain terpenes have also been included in detergent compositions at higher levels; for instance, DE—A—2,113,732 discloses the use of aliphatic and alicyclic terpenes as anti-microbial agents in washing compositions, while GB—A—1,308,190 teaches the
 45 use of dipentene in a thixotropic liquid detergent suspension base composition.

DE—A—2,709,690 teaches the use of pine oil (a mixture mainly of terpene alcohols) in liquid hard surface cleaning compositions. GB—A—2,033,491 discloses a composition for cleaning painting tools comprising a terpene and butanol. US—A—3,634,338 discloses an emulsion-form composition for cleaning
 50 metal surfaces comprising pine oil and cyclohexanol.

The present invention thus provides terpene-solvent mixtures useful for making liquid detergent compositions which are stable homogeneous fluent liquids having excellent suds control across the range of usage and water hardness conditions and which provide excellent shine performance together with improved cleaning characteristics both on greasy/oily soils and on inorganic particulate soils with little
 55 tendency to cause filming or streaking on washed surfaces.

According to the present invention there is provided a mixture useful for making a liquid detergent composition, the mixture consisting of (a) terpene selected from mono- and sesqui-terpenes and mixtures thereof, and (b) polar solvent, wherein the polar solvent is benzyl alcohol and wherein the weight ratio of
 60 terpene to polar solvent is from 5:1 to 1:5.

Preferred terpenes are mono- and bicyclic monoterpenes, especially those of the hydrocarbon class, which can be selected from terpinenes, terpinolenes, limonenes and pinenes. Highly preferred materials of
 65 this type include d-limonene, dipentene, α -pinene, β -pinene and the mixture of terpene hydrocarbons obtained from the essence of oranges (eg. cold-pressed orange terpenes and orange terpene oil phase extract). Terpene alcohols, aldehydes and ketones can also be used; however, the alcohols, in particular, provide valuable but unexpected improvements in viscosity regulation when incorporated in liquid detergent compositions at a level, preferably, of from 1% to 3%, more preferably from 1.5% to 2.5%. The

terpene is used in combination with benzyl alcohol. The liquid detergent compositions also preferably contain from 0.005% to 2%, more preferably from 0.05% to 0.7% of an alkali metal, ammonium or alkanolammonium soap of a C₁₃—C₂₄, especially C₁₃—C₁₈, fatty acid. Preferably, the fatty acid is fully saturated, for example, by hydrogenation of naturally occurring fatty acids. Addition of the soap, particularly to compositions containing terpene hydrocarbons, is found to provide significant synergistic enhancement in the suds-suppression effectiveness of the system.

A calcium sequestrant is also desirable in the liquid detergent compositions, providing not only cleaning advantages on particulate soil, but also, surprisingly, advantages in terms of product homogeneity and stability. The sequestrant component is a water-soluble inorganic or organic polyanionic sequestrant having a calcium ion stability constant at 25°C of at least 2.0 preferably at least 3.0, the weight ratio of surfactant:sequestrant preferably lying in the range from 5:1 to 1:3, especially 3:1 to 1:1. In preferred liquid detergent compositions, the sequestrant has an anion valence of at least 3 and is incorporated at a level of from 0.5% to 13% by weight. The liquid detergent composition itself preferably has a pH in 1% aqueous solution of at least 8.0.

Suitably, the sequestrant can be selected from the water-soluble salts of polyphosphates, polycarboxylates, aminopolycarboxylates, polyphosphonates and amino polyphosphonates and added at a level in the range from 1 to 9%, especially 2 to 8%, more especially 3 to 7% by weight of the liquid detergent composition. Adjustment of the sequestrant level and surfactant:sequestrant ratio within the above specified ranges is important for providing compositions of optimum stability.

A notable feature of the instant compositions is the suds-suppression effectiveness of the terpenes in liquid compositions based on ampholytic or zwitterionic surfactants. Thus, it is notoriously difficult to control the sudsing behaviour of these surfactants in a cost-effective manner using conventional suppression agents such as soaps, waxes etc. The terpenes are thus particularly valuable in this respect.

We will now discuss the individual components of the mixtures and detergent compositions in more detail.

A wide range of anionic, nonionic, zwitterionic and amphoteric surfactants can be used in the detergent compositions. A typical listing of the classes and species of these surfactants is given in US—A—3,663,961. These surfactants can be used singly or in combination at levels in the range from 1% to 20%, preferably at levels from 3% to 10% by weight of the detergent compositions.

Suitable anionic non-soap surfactants are water-soluble salts of alkyl benzene sulfonates, alkyl sulfates, alkyl polyethoxy ether sulfates, paraffin sulfonates, alpha-olefin sulfonates, alpha-sulfocarboxylates and their esters, alkyl glyceryl ether sulfonates, fatty acid monoglyceride sulfates and sulfonates, alkyl phenol polyethoxy ether sulfates, 2-acyloxy-alkane-1-sulfonate, and beta-alkyloxy alkane sulfonate. Of all the above, the paraffin sulfonates are highly preferred.

A particularly suitable class of anionic detergents includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl or alkaryl group containing from 8 to 22, especially from 10 to 20 carbon atoms and a sulfuric acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic detergents which form part of the detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈—C₁₈) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from 9 to 15, especially 11 to 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in US—A—2,220,099 and US—A—2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl group is 11.8 carbon atoms, abbreviated as C_{11.8}LAS.

Other anionic detergent compounds herein include the sodium C₁₀—C₁₈ alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain 8 to 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts or esters of α-sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from 10 to 18, especially 12 to 16, carbon atoms in the alkyl group and from 1 to 12, especially 1 to 6, more especially 1 to 4 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from 12 to 24, preferably 14 to 16, carbon atoms, especially those made by reaction with sulfur trioxide followed by neutralization under conditions such that any sultones present are hydrolysed to the corresponding hydroxy alkane sulfonates; water-soluble salts of paraffin sulfonates containing from 8 to 24, especially 14 to 18 carbon atoms, and β-alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo

processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred. Magnesium and calcium are preferred cations under circumstances described by BE—A—843,636. Mixtures of anionic surfactants are contemplated by this invention; a preferred mixture contains alkyl benzene sulfonate having 11 to 13 carbon atoms in the alkyl group or paraffin sulfonate having 14 to 18 carbon atoms and either an alkyl sulfate having 8 to 18, preferably 12 to 18, carbon atoms in the alkyl group, or an alkyl polyethoxy alcohol sulfate having 10 to 16 carbon atoms in the alkyl group and an average degree of ethoxylation of 1 to 6.

Suitable nonionic surfactants include alkoxyated nonionic surfactants and also those of a semi-polar character. Alkoxyated nonionic surfactant materials can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; nonylphenol and di-isooctylphenol condensed with 15 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 1 to 30 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 12, desirably between 3 and 9 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty and greasy soils, and in the presence of hardness sensitive anionic surfactants such as alkyl benzene sulfonates. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or, prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Dobanols and Neodols (Dobanol and Neodol are Trade Marks) which have about 25% 2-methyl branching (Dobanol and Neodol being Trade Names of Shell) or Synperonics (Synperonic is a Trade Mark), which are understood to have about 50% 2-methyl branching (Synperonic is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial (Trade Mark) by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45—4, Dobanol 45—7, Dobanol 45—9, Dobanol 91—3, Dobanol 91—6, Dobanol 91—8, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol (Trade Mark) series having from 9 to 15 carbon atoms in the alkyl group and up to 11, especially from 3 to 9, ethoxy residues per molecule.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with either propylene glycol or ethylene diamine. Such synthetic nonionic detergents are available on the market under the Trade Names of "Pluronic" and "Tetronic" respectively supplied by Wyandotte Chemicals Corporation (Pluronic and Tetronic are Trade Marks).

Of the above, highly preferred are alkoxyated nonionic surfactants having an average HLB in the range from 9.5 to 13.5, especially 10 to 12.5. Highly suitable nonionic surfactants of this type are ethoxylated primary or secondary C₉₋₁₅ alcohols having an average degree of ethoxylation from 3 to 9, more preferably from 5 to 8.

Suitable semi-polar surfactants are water-soluble amine oxides containing one alkyl moiety of from 10 to 28 carbon atoms and 2 moieties selected from alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms, and especially alkyl dimethyl amine oxides wherein the alkyl group contains from 11 to 16 carbon atoms; water-soluble phosphine oxide detergents containing one alkyl moiety of 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxide detergents containing one alkyl moiety of from 10 to 28 carbon atoms and a moiety selected from alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

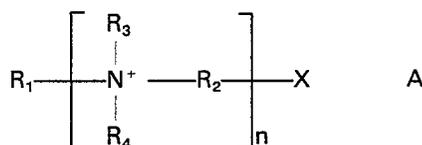
Suitable ampholytic surfactants are water-soluble derivatives of aliphatic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Suitable zwitterionic surfactants are water soluble derivatives of aliphatic quaternary ammonium

phosphonium and sulfonium cationic compounds in which the aliphatic moieties can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group.

Preferred amphoteric and zwitterionic surfactants have the general formula:—

5



10

wherein X is CO_2^- or SO_3^- , R_1 is an alkyl or alkenyl group having 8 to 22 carbon atoms, possibly interrupted by amide, ester or ether linkages, R_2 is a methylene, ethylene, propylene, isopropylene or isobutylene radical, R_3 and R_4 are independently selected from hydrogen, C_{1-3} alkyl or $-\text{R}_2-\text{X}$, wherein one of the substituents R_3 and R_4 is hydrogen if the other one is represented by the group $-\text{R}_2-\text{X}$, n is an integer from 1 to 6, and A is an equivalent amount of a neutralizing anion, except that amphoteric surfactants include amine salts of the above formula and also the corresponding free amines.

15

Highly preferred surfactants according to the above formula, include N-alkyl-2-aminopropionic acid, N-alkyl-2-imino-diacetic acid, N-alkyl-2-iminodipropionic acid, N-alkyl-2-amino-2-methyl-propionic acid, N-alkyl-propylenediamine-propionic acid, N-alkyl-dipropylenetriamine-propionic acid, N-alkyl-dipropylenetriamine dipropionic acid, N-alkylglycine, N-alkyl-amino-succinic acid, N-amidoalkyl-N'-carboxymethyl-N',N'-dimethyl-ammonio-ethylene diamine, N-alkyl-amino-ethane-sulfonic acid, N-alkyl-N,N-dimethyl-ammonio-hydroxy-propene-sulfonic acid and salts thereof, wherein alkyl represents a C_8 to C_{18} alkyl group, especially coconut alkyl lauryl and tallow alkyl. Specific examples include Armeen (Trade Mark) Z (marketed by Armour), Amphosol (Trade Mark) AA and SP (marketed by I.C.V.), Amphoram (Trade Mark) CP1, Diamphoram (Trade Mark) CP1, Triamphoram (Trade Mark) CP1, Triamphoram C_2P_1 and Polyamphorams (Trade Mark) CP1, C_2P_1 and C_3P_1 (marketed by Pierrefitte-Auby) and Deriphath (Trade Mark) 170C and Deriphath 154 (marketed by General Mills).

20

25

Of all the above surfactants, highly preferred compositions comprise as the single or major surfactant component, surfactants selected from the anionic, amphoteric and zwitterionic classes. The nonionic surfactants when present are preferably included in only a minor amount, i.e. at a level of 5 to 50% by weight of the surfactant system.

30

The sequestrant can be selected from the water-soluble salts of polyphosphates, polycarboxylates, aminopolycarboxylates, polyphosphonates and aminopolyphosphonates having a logarithmic calcium ion stability constant ($\text{pK}_{\text{Ca}^{++}}$) of about 2 or greater and preferably an anion valence of at least 3. The stability constant is defined as follows:—

35

$$\text{pK}_{\text{Ca}^{++}} = \log_{10} K_{\text{Ca}^{++}}$$

where

40

$$K_{\text{Ca}^{++}} = \frac{[\text{Ca}^{++} \text{A}^{(n-2)-}]}{[\text{Ca}^{++}][\text{A}^{n-}]}$$

45

and A^{n-} is the ionic species of sequestrant which predominates at the in-use pH of the composition (defined as the pH of a 1% aqueous solution of the composition) and n is at least 3.

Preferably, the sequestrant has a $\text{pK}_{\text{Ca}^{++}}$ in the range from 2 to 11, especially from 3 to 8. Literature values of stability constants are taken where possible (see Stability Constants of Metal-Ion Complexes, Special Publication No. 25, The Chemical Society, London); where doubt arises, the stability constant is defined at 25°C and at zero ionic strength using a glass electrode method of measurement as described in Complexation in Analytical Chemistry by Anders Ringbom (1963).

50

Suitable polyphosphates include pyrophosphates such as tetrasodium pyrophosphate decahydrate, and tetrapotassium pyrophosphate; tripolyphosphates such as pentapotassium tripolyphosphate; and higher polyphosphates and metaphosphates such as sodium pentapolyphosphate and sodium hexametaphosphate.

55

The carboxylate-type sequestrants can be described as monomeric polycarboxylate materials or oligomers or polymers derived from carboxylate or polycarboxylate monomers. The sequestrants can be acyclic, alicyclic or aromatic in nature.

Suitable polycarboxylates include the salts of citric acid, aconitic acid, citraconic acid, carboxymethyloxy succinic acid, lactoxysuccinic acid, and 2-oxa-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane-*cis, cis, cis*-tetracarboxylic acid, cyclopenta dienide pentacarboxylic acid, 2,3,4,5-tetrahydrofuran-*cis, cis, cis*-carboxylic acid, 2,5-tetrahydrofuran-*cis*-dicarboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB—A—1,425,343.

65

Suitable polymeric polycarboxylates include homo- and copolymers of polycarboxyl monomers such as maleic acid, citraconic acid, aconitic acid, fumaric acid, mesaconic acid, phenyl maleic acid, benzyl maleic acid, itaconic acid and methylene malonic acid; homo- and copolymers of acrylic monomers such as acrylic acid, methacrylic acid or α -hydroxy acrylic acid; or copolymers of one or more of the above
 5 polycarboxyl and acrylic monomers with another unsaturated polymerizable monomer, such as vinyl ethers, acrylic esters, olefins, vinyl pyrrolidones and styrenes.

Suitable aminopolycarboxylates include especially the amino polyacetates, e.g. sodium, potassium, ammonium and alkanolammonium ethylenediamine tetraacetates, diethylene triamine pentaacetates and nitrilotriacetates.

10 Polyphosphonate and aminopolyphosphonate materials suitable for use herein can be exemplified by nitrilo tri(methylene phosphonic acid), ethylenediamine tetra(methylene phosphonic acid), diethylene-triamine penta(methylenephosphonic acid) and the water-soluble salts thereof.

The terpene component of the present compositions belongs to the class of mono- or sesquiterpenes or mixtures thereof and can be acyclic or preferably monocyclic or bicyclic in structure. It is preferably
 15 liquid at room temperature (25°C). Preferred terpenes belong to the class of terpene hydrocarbons and terpene alcohols. Examples of acyclic terpene hydrocarbons suitable for use herein include 2-methyl-6-methylene-2, 7-octadiene and 2,6-dimethyl-2,4,6-octadiene. Preferred monocyclic terpene hydrocarbons belong to the terpinene, terpinolene and limonene classes, for example, the α , β and γ -terpinenes, the d and l-limonenes and dipentene (essentially a limonene racemate). The limonenes occur naturally in certain
 20 fruit and vegetable essences and a preferred source of limonene is the essence of orange and other citrus fruits. Preferred bicyclic terpene hydrocarbons include α and β -pinene. The terpene is added at a level of 0.5% to 10%, preferably 1% to 5% by weight of the detergent composition.

The terpene alcohol can be a primary, secondary or tertiary alcohol derivative of a cyclic or acyclic terpene hydrocarbon. Suitable tertiary alcohols include terpineol, usually sold commercially as a mixture of
 25 α , β and γ isomers and linalool; suitable secondary alcohols include borneol; suitable primary alcohols include geraniol. Complex mixtures of terpene alcohols are also suitable, especially the mixture of alcohols manufactured by distilling the oils extracted from pine wood, cones and needles and sold commercially as "pine oils". The terpene alcohol is preferably added at a level in the range from 1% to 3%, more preferably from 1.5% to 2.5% by weight of the detergent compositions in order to provide optimum control of product
 30 viscosity characteristics. Preferably such compositions have a viscosity in the range from 80 to 200 cp (0.08 to 0.2 Pa.s) measured in a Brookfield viscometer, using Spindle No. 2 at 60 r.p.m. and at 21°C.

The polar solvent component of the present compositions is benzyl alcohol. The solvent can be at a level of 0.5% to 10%, especially 1% to 5%, by weight of the detergent composition and is used at a weight ratio of terpene:solvent in the range from 5:1 to 1:5, especially 2:1 to 1:2.

35 The detergent compositions can be supplemented by all manner of detergent components compatible with a fluent, liquid system.

A non-aqueous solvent is a particularly suitable additional ingredient, especially water miscible or highly soluble (at least 20% w/w) aliphatic mono-, di- and tri alcohols. Specific examples are ethanol, propanol, isopropanol, and propane-1,3-diol. Other suitable solvents are ethylene-, propylene-, diethylene-
 40 and dipropylene glycol and the mono- C_{1-4} alkyl ether and C_{1-4} ester derivatives thereof such as the ethylene glycol monomethyl-, monoethyl- and monobutyl ethers, propylene glycol propyl ether, dipropylene glycol methyl ether, ethylene glycol mono acetate and ethylene glycol monoethyl ether acetate. The non-aqueous solvent can be added in amounts up to 10%, preferably 6% by weight of the detergent composition.

45 Hydrotropes such as urea, monoethanolamine, diethanolamine, triethanolamine and the sodium, potassium, ammonium and alkanol ammonium salts of xylene-, toluene-, ethylbenzene-, isopropylbenzene sulfonates, can also be added to the detergent compositions in amounts up to 10% by weight. It is a feature of the present invention, however, that stable, homogenous formulations can be prepared without the need for hydrotropic materials of this kind, or with only very minor levels (i.e. less than 4% by
 50 weight).

Other suitable ingredients of the present compositions include pH buffering materials such as alkali metal and ammonium carbonates, bicarbonates, metasilicates and ortho phosphates. These can be added, if appropriate, at levels up to 10% by weight to provide a compositional pH equal to or greater than pH 8, preferably greater than pH 9 and more preferably greater than pH 10. Dyes, perfumes enzymes,
 55 chlorine-releasing agents, polypeptides and protein hydrolysates, soil suspending agents such as carboxy methylcellulose, hydroxymethyl cellulose and polyethylene glycols having a molecular weight of 400 to 10,000, fluorescers such as disodium 4,4'-bis(2-morpholino-4-anilino-s-triazin-6-yl amino) stilbene-2,2'-disulfonate, preservatives such as Preventol (Trade Mark) ON marketed by Bayer, thickeners such as xanthan gum, and additional suds regulants such as tributylphosphate and silicone oil can all be included
 60 in the detergent compositions.

A germicide such as o-phenyl phenate can also be added to the detergent compositions, providing excellent hard surface germicidal activity.

In the examples which follow, the abbreviations used have the following descriptions:—

O 106 266

	PS	Sodium C ₁₃ to C ₁₆ paraffin sulfonate marketed by Hoechst under Trade Name Hostapur SAS.
5	LAS	Sodium salt of linear C _{11.8} alkyl benzene sulfonate.
	Dobanol 91—8	A C ₉₋₁₁ oxo-alcohol with 8 moles of ethylene oxide, marketed by Shell.
	Deriphath 170C	N-C ₁₂₋₁₄ alkyl-β-amino propionic acid marketed by General Mills.
10	Deriphath 154	Disodium-N-tallow-β-amino propionate marketed by General Mills.
	CN Soap	Monoethanolamine soap of coconut fatty acids.
	TEA	Triethanolamine.
15	CS	Sodium cumene sulfonate.
	TPP	Tetrasodium pyrophosphate.
	EDTA	Tetrasodium salt of ethylenediamine tetraacetic acid.
	NTA	Trisodium salt of nitrilotriacetic acid.

20

Examples 1 to 4

The following liquid compositions were prepared by mixing the ingredients in water:—

		1	2	3	4
25	PS	4.5	—	8.0	—
	LAS	—	4.0	—	4.0
30	Dobanol 91—8	2.0	—	—	2.0
	Sodium citrate · 2H ₂ O	3.5	—	—	—
	Sodium metasilicate	—	—	3.0	—
35	Sodium carbonate	3.0	2.5	—	—
	EDTA	—	—	2.5	—
40	NTA	—	3.0	—	6.0
	Orange terpenes	2.0	—	—	—
	Dipentene	—	2.0	—	—
45	D-limonene	—	—	6.0	—
	β-pinene	—	—	—	3.0
50	Benzyl alcohol	2.0	2.0	6.0	1.5
	Ethanol	—	—	2.0	—
	CS	2.0	2.0	3.0	2.0
55	Water, perfume & minors	————— To 100 —————			

60 The above compositions were homogeneous fluent liquids having good stability, excellent surface-shine and cleaning characteristics on both inorganic particulate soils and oily/greasy soils with controlled sudsing in both dilute and concentrated usage under both hard and soft water conditions.

65

O 106 266

Examples 5 to 6

		5	6
5	PS	8.0	4.0
	Sodium citrate · 2H ₂ O	—	3.0
	Sodium metasilicate	3.0	—
10	Sodium carbonate	—	3.0
	EDTA	2.5	—
15	Orange terpene	—	2.0
	Dipentene	6.0	—
	Benzyl alcohol	6.0	1.5
20	CN Soap	1.5	0.3
	Xanthan gum	—	0.5
25	Ethanol	2	—
	TEA	3.0	—
	CS	—	2.0
30	Water, perfume & minors	— To 100 —	

35 The above compositions were homogeneous fluent liquids having good stability, excellent surface shine and cleaning characteristics on both inorganic particulate soils and oily/greasy soils with controlled sudsing in both dilute and concentrated usage under both hard and soft water conditions.

40

45

50

55

60

65

0 106 266

Examples 7 to 9

		7	8	9
5	LAS	—	—	1.0
	Dobanol 91—8	2.0	2.0	—
	Deriphath 170C	5.0	2.5	—
10	Deriphath 154	—	1.0	4.0
	CN Soap	—	—	0.5
15	Sodium citrate · 2H ₂ O	—	—	8.0
	TPP	4.0	—	—
	Benzyl alcohol	2.0	3.0	2.0
20	CS	5.0	7.0	2.0
	Orange terpenes	—	—	2.5
25	α-pinene	2.0	—	—
	Terpinolene	—	5.0	—
	Ethanol	—	2.0	—
30	Water, perfume & minors	——— To 100 ———		

35 The above compositions were homogeneous fluent liquids having good stability, excellent cleaning characteristics on both inorganic particulate soils and oily/greasy soils with controlled sudsing in both dilute and concentrated usage under both hard and soft water conditions.

Examples 10 to 12

		10	11	12
40	PS	4.5	5.0	1.0
	LAS	—	—	2.0
45	Dobanol 91—8	—	—	0.5
	Sodium citrate · 2H ₂ O	3.5	3.5	—
50	Sodium carbonate	3.0	2	6.0
	Pine oil	2.0	—	—
	α-terpineol	—	1.8	—
55	Linalool	—	—	2.2
	Benzyl alcohol	1.5	1.5	4.0
60	o-Phenyl phenate	1.3	1.5	1.3
	CS	1.4	1.5	1.0
65	Water, perfume and minors	——— To 100 ———		

0 106 266

The above compositions were homogeneous, fluent liquids having good stability at both normal and low temperatures, as well as excellent germicidal activity, surface shine and cleaning performance on both inorganic particulate soils and oily/greasy soils.

5 Claims

1. A mixture useful for making a liquid detergent composition, the mixture consisting of:
 - a) terpene selected from mono- and sesqui-terpenes and mixtures thereof, and
 - b) polar solvent, wherein the polar solvent is benzyl alcohol and wherein the weight ratio of terpene to polar solvent is from 5:1 to 1:5.
2. A mixture according to Claim 1 wherein the terpene is selected from orange terpenes.
3. A mixture according to Claim 1 or 2 wherein the weight ratio of terpene to polar solvent is from 2:1 to 1:2.

15 Patentansprüche

1. Ein zur Herstellung einer flüssigen Reinigungsmittelzusammensetzung verwendbares Gemisch, bestehend aus:
 - (a) Terpen, ausgewählt aus Mono- und Sesqui-terpenen, und Mischungen davon, und
 - (b) polarem Lösungsmittel, wobei das polare Lösungsmittel Benzylalkohol ist, und wobei das Gewichtsverhältnis von Terpen zu polarem Lösungsmittel 5:1 bis 1:5 beträgt.
2. Ein Gemisch nach Anspruch 1, wobei das Terpen aus Orangerterpenen ausgewählt ist.
3. Ein Gemisch nach Anspruch 1 oder 2, wobei das Gewichtsverhältnis von Terpen zu polarem Lösungsmittel 2:1 bis 1:2 beträgt.

25 Revendications

1. Mélange utile pour préparer une composition détergente liquide, le mélange étant constitué:
 - a) de terpène choisi parmi les mono-terpènes et les sesqui-terpènes et leurs mélanges, et
 - b) d'un solvant polaire, dans lequel le solvant polaire est l'alcool benzylé et dans lequel le rapport pondéral du terpène au solvant polaire est de 5:1 à 1:5.
2. Mélange selon la revendication 1, dans lequel le terpène est choisi parmi les terpènes d'orange.
3. Mélange selon la revendication 1 ou 2, dans lequel le rapport pondéral du terpène au solvant polaire est de 2:1 à 1:2.

35

40

45

50

55

60

65