1) Publication number:

0 105 063

**B1** 

(12)

# **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification: 30.12.86

(i) Int. Cl.4: **C 11 D 3/43**, C 11 D 17/00

(2) Application number: 82305211.3

(2) Date of filing: 30.09.82

(54) Liquid hard-surface cleaner.

- Date of publication of application: 11.04.84 Bulletin 84/15
- 4 Publication of the grant of the patent: 30.12.86 Bulletin 86/52
- M Designated Contracting States: BE DE FR GB IT NL
- References cited: EP-A-0 040 882 DE-B-2 709 690 FR-A-2 390 499

73 Proprietor: THE PROCTER & GAMBLE COMPANY
301 East Sixth Street
Cincinnati Ohio 45202 (US)

Inventor: Diez, Ricardo
2241 Ingersoll Drive
Burlington Ontario L7P 3L1 (CA)
Inventor: Compton, Donald Brown
2288 Courtland Drive
Burlington Ontario L7R 1S6 (CA)
Inventor: Fraser, Neil David
6115 Southlands Place
Vancouver British Columbia V6N 1M9 (CA)
Inventor: Burns, Michael Eugene
9248 Sunderland Way
West Chester Ohio 45069 (US)

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

30

35

40

45

55

60

This invention relates to novel homogeneous aqueous liquid detergent compositions intended for general purpose household usage for cleaning hard surfaces.

Compositions intended for such purposes have been commercially manufactured for many years. They have been available in both liquid and granular form, and often have been formulated to perform especially well in accomplishing some specific household task, such as cleaning tile floors in kitchen and bath, or tile walls in the bath, or bathroom tubs, or kitchen sinks, or painted walls in the kitchen or elsewhere in the house, or glass and porcelain surfaces. In general, the requirements for these tasks differ sufficiently from one another that no single composition is ideal for all such usages. The compositions of the present invention are effective across an unusually broad spectrum of these tasks.

Products sold commercially for use in cleaning hard surfaces around the house fall into several categories. Solvent-based liquids such as Pine Sol (TM American Cyanamid Co.) and Lestoil (TM Noxell Corp.) typically contain about 25 to 35% of a solvent such as pine oil together with about 10—15% surfactant, but with little or no sequestering builders or alkaline buffers. When used full strength they are effective on greasy soils, such as spots on kitchen walls, but clean poorly on bathroom soils. They are also poor when diluted with water for cleaning surfaces having a broad area such as floors or walls.

Built products have been formulated as both granules and liquids. The former contain large amounts of sequestering builders and alkaline buffers, with generally low levels of surfactant and no solvent. They are especially effective when dissolved and used on broad wall or floor surfaces, but are somewhat less effective as compared with other types of formulations in those applications where concentrated product is needed. Liquid products of this type, such as Mr. Clean (TM Procter & Gamble Inc.), typically contain up to about 18% builder, up to about 5% surfactant, and up to about 12% hydrotrope, with little or no solvent—perhaps levels up to 2% or thereabouts.

Other formulations such as Windex (TM Drackett Company), Fantastik (TM Texize Chemicals, Inc.) and Formula 409 (TM Chlorox Co.) have been prepared for use as spray cleaners on glass or appliances where freedom from streaking is an important advantage because rinsing is not normally done. These products may also be used full strength for spots on walls. They typically contain from about 4% to about 7% solvent, about 1—10% surfactant, and about 1—3% sequestering builder/alkaline buffer.

Still other formulations such as Comet (TM Procter & Gamble Inc.) are sold as abrasive cleansers for use on sinks, tubs and the like. They are most commonly in dry form, and contain finely ground silica as abrasive, together with relatively low levels of chlorine bleach, surfactant, calcium sequestrant, and alkaline buffer. A liquid cleanser containing suspended abrasive has also appeared commercially. These cleanser formulations contain no solvent.

Documents that make reference to liquid detergent compositions containing surfactants, builders and selected solvents, at levels that are high for the prior art but low as compared with these of the present invention, include US—A—3,232,880 US—A—3,360,476, US—A—4,175,062, EP—A—40882 and DE—B—2709690, the latter describing liquid detergents, comprising surfactants, sodium tripolyphosphate ethyleneglycolmonobutylether, pine oil, and sodium cumene sulfonate.

A recent publication [JP—A—56-22397 laid open for public inspection on March 2, 1981 in the name of Tanigawa Yuka Kogyo K.K.] has disclosed liquid detergent compositions for the bathroom containing relatively large amounts of aminocarboxylate builders, and glycol ether solvents used with small amounts of surfactant. Amounts of these ingredients exemplified by Tanigawa are respectively, on a weight basis, approx. 10—12%; 7—8%; and 2%.

The gist of the present invention is a range of compositions in convenient liquid form which contain exceptionally high levels of both builders and of solvents specifically chosen for their superb cleaning abilities, together with surfactant and with other ingredients needed to make the compositions homogeneous and physically stable for convenient use and storage. The compositions of this invention are novel and exhibit outstanding performance characteristics that have not hitherto been achieved in a single formula: cleaning of floors as well as commercial liquid or granular floor cleaners when both are used diluted; cleaning of greasy walls as well as commercial wall cleaners when both are used full strength; and cleaning of bathtub soil, when used full strength, as well as abrasive cleansers.

## Disclosure of invention

The detergent compositions of the present invention are homogeneous aqueous liquids comprising the following components:

- a) from 0.9% to 10% of a non-soap anionic, amphoteric, zwitterionic or nonionic surfactant;
- b) from zero to 5% soap;
- c) from 10.5% to 19% of an alkali metal polyphosphate or polyphosphate sequestrant;
- d) from zero to 6% of an alkaline pH buffer, with the proviso that the sum of components (c) and (d) is not greater than 21% of the composition;
- e) from 6% to 15% of a Principal Solvent having a molar volume below 200 (cm³/g mol) and solubility parameters at 25°C, as follows: Polarity Parameter from 0 to 7.16 (J/cm³)¹/² and Hydrogen Bonding Parameter from 0 to 12.28 (J/cm³)¹/²;
- 5 f) from zero to 10% of an Auxiliary Solvent having a Polarity Parameter of 7.18 (J/cm<sup>3</sup>)<sup>1/2</sup> or above

and/or a Hydrogen Bonding Parameter of 12.30 (J/cm<sup>3</sup>)<sup>1/2</sup> or above, with the proviso that the sum of components (e) and (f) is not greater than 22% of the composition;

g) from 3% to 25% of a hydrotrope; and

h) the balance water; wherein all percentages are by weight of the composition; and wherein the pH of a 1% aqueous solution of the detergent composition is from 8.5 to 11.

#### Surfactants

15

The surfactants of this invention are of two general types, each of which characterized separately herein. The first such type is comprised of a wide range of non-soap anionic, zwitterionic, amphoteric and nonionic surfactants. A typical listing of the classes and species of these surfactants is given in US—A—3,664,961. These surfactants can be used singly or in combination at levels in the range from 0.9% to 10%, preferably at levels from 2% to 7% by weight of the compositions.

Non-soap surfactants as herein defined contribute cleaning performance to the compositions of this invention, especially when used in diluted form to clean broad surfaces such as floors and walls.

Suitable anionic non-soap surfactants are water-soluble salts of alkyl benzene sulfonates, alkyl sulfates, alkyl polyethoxy 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.

A particularly suitable class of non-soap anionic detergents includes water-soluble 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 sulfonic 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 (C<sub>10</sub>—C<sub>18</sub>) carbon atoms produced from 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 preferred from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminum 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 about 11.8 carbon atoms, abbreviated as C<sub>11.8</sub>LAS.

Other non-soap anionic detergent compounds herein include the sodium  $C_{10}$ — $C_{18}$  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 non-soap anionic detergent compounds herein include the water-soluble salts or esters of alpha-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 polethoxy 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 moieties of ethylene oxide per fatty alcohol moiety; 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 beta-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 or alkanol-ammonium cations; or magnesium or calcium cations under circumstances described by CA—A—1,071,055.

Mixtures of non-soap anionic surfactants are contemplated by this invention; a preferred mixture contains alkyl benzene sulfonate having 11 to 13 carbon atoms in the alkyl group and either an alkyl sulfate having 8 to 18, preferably 12 to 18, carbon atoms in the alkyl group, or an alkyl polyethoxy sulfate having 10 to 16 carbon atoms in the alkyl group and an average degree of ethoxylation of 1 to 6.

Suitable ampholytic surfactants are water-soluble derivatives of aliphatic secondary and tertiary amines in which the aliphatic moiety is 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 are 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

35

$$R_{1} - \begin{bmatrix} R_{3} \\ | \\ -N^{+} - R_{2} - \\ | \\ R_{4} \end{bmatrix} - X \qquad A$$

wherein X is CO<sub>2</sub><sup>-</sup> or SO<sub>3</sub><sup>-</sup>, R<sub>1</sub> is alkyl or alkenyl group having 8 to 22 carbon atoms, possibly interrupted by amide, ester or ether linkages, R<sub>2</sub> is a methylene, ethylene, propylene, isopropylene or isobutylene radical, R<sub>3</sub> and R<sub>4</sub> are independently selected from hydrogen, C<sub>1-3</sub> alkyl or —R<sub>2</sub>—X, whereby one of the substituents R<sub>3</sub> and R<sub>4</sub> is hydrogen if the other one is represented by the group —R<sub>2</sub>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.

Highly preferred surfactants according to the above formula include N-alkyl-2-aminopropionic acid, N-alkyl-2-imino-diacetic acid, N-alkyl-2-imino-diacetic acid, N-alkyl-2-imino-diacetic acid, N-alkyl-2-imino-diacetic acid, N-alkyl-2-imino-diacetic acid, N-alkyl-2-imino-2-methyl-propionic acid, N-alkyl-dipropylene-triamine-propionic acid, N-alkyl-dipropylene-triamine-propionic acid, N-alkyl-dipropylene-triamine-propionic acid, N-alkyl-dipropylene-triamine-propionic acid, N-alkyl-dipropylene-triamine-propionic acid, N-alkyl-dipropylene-triamine-propionic acid, N-alkyl-amino - succinic acid, N-alkyl-amino - succinic acid, N-alkyl-amino - succinic acid, N-alkyl-amino - ethane - sulfonic acid, N-alkyl-amino - succinic acid, N-alkyl-dipropylene-triamino-propionic acid, N-alkyl-dipropyl

Suitable nonionic surfactants are of several classes. Suitable semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from 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 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 the group consisting of alkyl and hydroxalkyl moieties of from 1 to 3 carbon atoms.

Another and especially suitable class of nonionic surfactants are alkyl mono- and di-alkanol amides, the alkyl group of which contains from 10 to 18 carbon atoms, such as coconut monoethanol amide and oleyl diethanol amide. Particularly preferred are the  $C_{10}$  to  $C_{18}$ , more especially  $C_{12}$  to  $C_{14}$ , diethanol amides.

Alkoxylated nonionic surfactants are another class that is suitable for use in this invention, especially when used in mixtures at levels no more than 50% of the total non-soap surfactant system, preferably at levels from 5% to 35% thereof. Alkoxylated 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 (a) 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 reacted with ethylene oxide in amounts equal to from 1 to 25 mols of ethylene oxide per mol 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 3 mols of ethylene oxide per mol of phenol; dinonylphenol condensed with 10 mols of ethylene oxide per mol of phenol; and nonylphenol and di-isooctylphenol condensed with 20 mols of ethylene oxide; (b) The condensation products 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 mols of alkylene oxide per mol 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 mols of ethylene oxide per mol of aliphatic alcohol. Preferred nonionic surfactants of this type 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 (RTM) and Neodols (RTM) which have about 25% 2-methyl branching (Dobanol (RTM) and Neodol (RTM) being Trade Names of Shell Chemical Co.) or Synperonics (RTM), which are understood to have about 50% 2-methyl branching (Synperonic (RTM) is a Trade Name of Imperial Chemical Industries Ltd.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquigas S.p.A. Specific examples of nonionic surfactants include Dobanol (RTM) 45-4, Dobanol (RTM) 45-7, Dobanol (RTM) 45-9, Dobanol (RTM) 91-3, Dobanol (RTM) 91-6, Dobanol (RTM) 91-8, Synperonic (RTM) 6, Synperonic (RTM) 14, the condensation products of coconut alcohol with an average of between 5 and 12 mols of ethylene oxide per mol 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 mols of ethylene oxide per mol 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 (TM Union Carbide Corp.) 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; and (c) block polymers 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 commercially available under the names "Pluronic" and "Tetronic", respectively [TM BASF Wyandotte Corp].

Of the above, preferred alkoxylated nonionic surfactants have an average HLB (hydrophilic-lipophilic balance) in the range from 9.5 to 13.5, especially from 10 to 12.5. Highly suitable nonionic surfactants of this type are ethoxylated primary or secondary  $C_{9-15}$  alcohols having an average degree of ethoxylation from 3 to 9.

Especially preferred non-soap surfactants are  $C_{10-18}$  alkyl diethanol amide and the sodium salts of straight or branched chain  $C_{9-15}$  alkyl benzene sulfonate,  $C_{10-18}$  alkyl sulfate, and  $C_{10-18}$  alkyl polyethoxy sulfate containing from 1 to 12 ethylene oxide moieties per fatty alcohol moiety.

Soaps are specifically excluded from the surfactants disclosed hereinabove. However, soaps derived from fatty acids, natural or synthetic, saturated or unsaturated, having alkyl chains ranging from about 10 to 18 carbon atoms in length, are also useful in the compositions of the present invention. Examples of preferred soaps are sodium and potassium laurate, myristate, palmitate, oleate and stearate; and sodium and potassium soaps derived from coconut and tallow fatty acids.

Soaps are effective not only as supplemental cleaning agents, but also aid in the solublization of other ingredients of the composition. In addition they control sudsing, which is highly desirable for compositions that are intended to not require rinsing. Accordingly, use of from 0.5% to 5% soap is preferred in the compositions of this invention. This usage is, however, by no means essential to obtain superb cleaning performance characteristics and the requisite product homogeneity, and the broad limits of soap usage are therefore from zero to 5%.

#### **Builders**

30

40

The builders of this invention are of two general types, each of which is characterized separately herein. Materials useful as Sequestrants are hardness sequestering builders selected from the alkali metal salts of polyphosphates and polyphosphonates.

Sequestrants are used in amounts from 10.5% to 19% by weight of the composition, preferably from 12% to 16%. It has been found that amounts up to 10.5% do not fully meet the multipurpose cleaning objectives of this invention while amounts over 19% are unnecessary to meet these objectives, difficult to solubilize, and add to costs not only directly but also indirectly by increasing hydrotrope requirements.

Polyphosphonates suitable for use herein can be exemplified by the Na, K and Li salts of methylene diphosphonic acid; ethylene diphosphonic acid; ethane-1, 1,2-triphosphonic acid; and ethane-1-hydroxy-1,1-diphosphonic acid.

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. Among preferred Sequestrants can be mentioned and alkali metal salts, more particularly the sodium and potassium salts, of pyrophosphoric acid and tripolyphosphoric acid. Especially preferred is the potassium salt of pyrophosphoric acid.

Alkaline pH Buffers are a second type of builder. These materials include alklia metal carbonate, bicarbonate, orthophosphate, borate and silicate salts and ethanolamines. Buffers are not essential ingredients of the compositions of this invention. However they are preferably used in amounts from 0.5% to 6% by weight of the composition to provide a source of reserve alkalinity. They are selected according to the conventional wisdom of the detergent arts to provide pH buffering from 8.5 to 11.0 for a 1% aqueous solution of the complete composition of this invention. The lower pH boundary was selected in relation to cleaning effectiveness and the upper boundary in relation to mildness and safety to surfaces.

So long as the composition has the proper pH as defined herein, it is an effective cleaner without the presence of buffer for soils that do not contain an acidic component.

Accordingly the broad limits for buffer are zero to 6% by weight of the composition. There is a further limitation that the total of Sequestering Builder plus pH Buffer be not greater than 21% by weight of the composition; this limitation is in relation to solubilization requirements for the homogeneous liquids of this invention.

# Solvents

65

The solvents of this invention are of two types that are characterized separately herein. The first is a Principal Solvent that is required to meet the detergency objectives. The second is an Auxiliary Solvent that under certain circumstances as described herein is utilized to solubilize the Principal Solvent in the composition in order to prepare a clear, homogeneous finished product.

The Principal Solvent of this invention is used in an amount from 6% to 15% by weight of the

composition, preferably from 8% to 12%, more preferably from 10% to 12%. It has the following physical properties at 25°C:

Molar volume:

below 200(cm<sup>3</sup>/g mol)

Solubility parameters:

Polarity parameter: Hydrogen bonding parameter: 0 to 7.16  $(J/cm^3)^{1/2}$ 0 to 12.28  $(J/cm^3)^{1/2}$ 

The molar volume of a compound is the quotient of its molecular weight divided by its density. This has metric units of (grams per g. mol) divided by (grams per cubic centimeter) which results in a unit of volume per gram mol of the compound in question.

The solubility parameters defined above are those of Hansen and Beerbower, "Solubility Parameters", Kirk-Othmer Encyclopedia of Chemical Technology, second ed., Supplementary Volume pp. 889—910, John Wiley & Sons, N.Y. (1971). Hansen characterized the solubility behavior of liquids according to three modes of interaction between molecules: (1) dispersion (London) forces arising from fluctuating atomic dipoles caused by electrons rotating about a nucleus; (2) interaction between permanent or induced molecular dipoles; and (3) hydrogen bonds. These are frequently identified as  $\delta_D$ ,  $\delta_P$  and  $\delta_H$  respectively, and are herein designated by the terms dispersion parameter, polarity parameter, and hydrogen bonding parameter, respectively.

A listing of these four parameters at 25°C. for over 200 solvents appears as Table 1, of Hansen et al op. cit. The criteria for the Principal Solvents of the present invention have been selected as follows: Solvents having molar volumes above 200 are so large that they do not penetrate and disperse soils rapidly and well. A solvent's dispersion parameter has been found inconsequential to detergent effectiveness. However, it has been determined that the Polarity and Hydrogen Bonding Parameters of a solvent must be lower than 7.16 and 12.28 (J/cm³)<sup>1/2</sup> respectively, to provide the superb detergency properties across the great variety of detergency applications that this invention is intended to accomplish. Mixtures of Principal Solvents having molar volumes and solubility parameters within the range defined above are also suitable for use in the instant invention.

It has further been found that solvents having Polarity Parameters and/or Hydrogen Bonding Parameters at or below 4.09 (J/cm³)¹¹² while they perform superbly as cleaners in the compositions of the present invention, are often not sufficiently miscible with the other ingredients to form clear, stable, homogeneous liquid compositions, even with the addition of hydrotropes as hereinafter defined. Accordingly, Auxiliary Solvents having Polarity and/or Hydrogen Bonding Parameters higher than 7.18 and 12.30 (J/cm³)¹², respectively (i.e. higher than the limits defined hereinbefore for the Principal Solvent), can be added to compatibilize the Principal Solvents in these compositions. As a guide to formulation, each parameter of a solvent mixture can be estimated according to the weighted average of its components.

The Auxiliary Solvents of this invention can be used in an amount up to 10% of the composition by weight, i.e. from zero to 10%. When used, preferred amounts are from 2% to 10% by weight of the composition. Because of solubilization requirements, the total of Principal Solvent plus Auxiliary Solvent should not be greater than 22% of the composition by weight.

When the Polarity and Hydrogen Bonding Parameters of the Principal Solvent are both above 4.09 (J/cm³)<sup>1/2</sup>, an Auxiliary Solvent is in general not necessary for solubilization and preferably is used in an insignificant amount if at all; i.e. less than 2% by weight of the composition.

Auxiliary solvents used in this manner have sometimes been described in the prior art as "coupling agents". This term is avoided herein, as the solubilizing function can often be accomplished not only by Auxiliary Solvents as defined herein, but also by Principal Solvents of relatively high Polarity and Hydrogen Bonding Parameters. So doing not only accomplishes the solubilizing function but also contributes effectively to cleaning. According to these principles, it may be preferred, for example, to solubilize xylene with diethylene glycol mono-n-butyl ether than with isopropyl alcohol.

Examples of how solvents meet these definitions are as follows:

55

5

60

5	Code	Solvent	Molar volume cm³ g mol	Polarity parameter J 1/2 cm <sup>3</sup>	Hydrogen bonding parameter J 1/2 cm <sup>3</sup>	
-	, A	Dodecane	228	0	0	_
	В	Toluene	106	1.43	2.05	
10	С	Naphthalene	112	2.05	5.93	
	D	Isopropyl alcohol	77	6.14	16.37	
15	Е	Glycerol ·	73	12.07	29.26	
	F	Hexylene glycol	123	8.39	17.80	
	G	Propylene carbonate	85	18.01	4.09	
20	Н	Ethylene glycol monoethyl ether	98	9.21	14.32	
25	1	Diethylene glycol mono-n-butyl ether	170	6.96	10.64	
	J	Butyl acetate	133	3.68	6.34	
	K	Pine oil	~126	~4.09	~11.46	
30	L	Orange terpene	~154	~0	~0.61	

Discussing these solvents individually:

35

40

The molar volume of dodecane is too high to satisfy the requirements of this invention as to A. Principal Solvent.

B.C. Toluene or naphthalene can be used as Principal Solvent, but require the addition of an Auxiliary Solvent to satisfy the solubility requirements of this invention.

D,E,F,G,H. Isopropyl alcohol, hexylene glycol, glycerol, propylene carbonate and ethylene glycol monoethyl ether are too high in Polarity Parameter and/or Hydrogen Bonding Parameter to satisfy the requirements of Principal Solvent. However they are acceptable as Auxiliary Solvents.

Diethylene glycol mono-n-butyl ether can be used as Principal Solvent of this invention. I,J,K,L.

In the foregoing table, parameters for solvents A-J are those appearing in Hansen et al. op. cit. Parameters for solvents K and L were estimated, as follows:

Pine oil, according to the Pine Oil Formulary, Hercules Powder Company ca. 1963, is derived from extracts of pine wood and is comprised predominantly of cyclic terpene alcohols. Its chief constituent is alpha terpineol, a tertiary alcohol having the structure ØC(CH<sub>3</sub>)<sub>2</sub>OH, which is present at levels ranging from below 70% to as high as 85%, depending upon the commercial grade, with the remainder being a mixture of terpene hydrocarbons, ethers and ketones. Values for the molar volume, Polarity Parameter and Hydrogen Bonding Parameter of alpha terpineol and pine oil are not available in the literature. However, based on literature values for chemicals of closely related structure and upon cleaning data, these three values are estimated for both substances to be approximately those appearing in the foregoing table for solvent K.

Orange terpenes and limonenes, also, are mixtures of chemicals derived from naturally occurring materials that vary somewhat according to source. These three values for both substances are estimated to be approximately those appearing in the foregoing table for solvent L.

It will be understood that selection of Principal Solvents and Auxiliary Solvents for particular applications of this invention will take into consideration not only the parameters discussed hereinabove but also such usual criteria as cost, availability, odor, flammability, safety, etc.

Solvents meeting the criteria herein expressed for Principal Solvents of this invention, that ordinarily do not require the use of Auxiliary Solvents, include ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, isopropylene glycol mono ethyl ether, isopropylene glycol mono propyl ether, isopropylene glycol mono butyl ether, methyl cyclohexane, butyl acetate, amyl acetate, butyl butyrate, butyl lactate, diethyl 65 carbonate, diethyl succinate, methyl i-amyl ketone, morpholine, and anisole.

Solvents meeting the criteria herein expressed for Principal Solvents of this invention, for which Auxiliary Solvents are ordinarily required, include n-hexane, n-decane, cyclohexane, toluene, xylene, naphthalene, diethyl benzene, chlorobenzene, trichloroethylene, pine oil, alpha terpineol, d-limonene, and orange terpene.

Solvents which can be used as Auxiliary Solvents in this invention, that do not meet the criteria for Principal Solvents, include propylene carbonate, methyl ethyl ketone, acetone, ethylene glycol mono methyl ether, ethylene glycol mono ethyl ether, diethylene glycol mono methyl ether, diethylene glycol mono ethyl ether, benzyl alcohol, diethylene glycol, glycerol, hexylene glycol, propylene glycol, ethylene glycol, 1-butanol, 1-propanol, and ethanol.

The foregoing lists are not intended to be exhaustive but rather to exemplify the varied kinds of solvents that meet the parameters of this invention as defined hereinbefore. Provided solvents meet the molar volume, polarity parameter and hydrogen bonding parameter limits as hereinbefore defined, the Principal Solvents of this invention can be selected from among aliphatic, aromatic and chlorinated hydrocarbons; alcohols; esters; ethers; glycol ethers; ketones; and amines.

Preferred Principal Solvents are ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol, mono-n-hexyl ether, isopropylene glycol mono ethyl ether, mixed isopropylene glycol mono-butyl, ethyl and propyl ethers, pine oil, alpha terpineol, orange terpene, methyl cyclohexane, toluene, xylene, butyl acetate and amyl acetate. Especially preferred is diethylene glycol mono-n-butyl ether, used in the essential absence of an Auxiliary Solvent.

## Hydrotrope

5

20

Solubilization of ingredients of dissimilar characteristics such as solvents and electrolytes is achieved by the use of hydrotropes. Water soluble salts of low molecular weight organic acids are suitable hydrotropes. Among such materials are sodium and potassium salts of toluene, benzene and cumene sulfonic acids, and sodium and potassium sulfosuccinate. Urea is also a suitable hydrotrope. Hydrotropes are used in amounts from 3% to 25% by weight of the composition, preferably from 6% to 14%.

## Optional ingredients

The compositions of the present invention can optionally contain minor amounts of colorants; perfumes; soil suspending agents such as carboxymethyl cellulose, sodium polyacrylate, and polyethylene glycols having a molecular weight from 400 to 10,000; fluorescers; suds boosters; suds regulants; opacifiers; enzymes and enzyme stabilizers; germicides; antioxidants such as sodium sulfite; and other materials known to the liquid detergent arts. Among the latter are chelating agents for heavy metals such as nitrilotriacetic acid, ethylene diamine tetraacetic acid and N-hydroxyethyl ethylene diamine triacetic acid, added in the form of free acids or alkali metal salts thereof; in quantities so low as to make a negligible contribution as hardness sequestering builder (e.g. at or below 1% by weight of the compositions); for the purpose of improving the clarity and/or color stability of the liquid product.

## Industrial application

The following examples describe the formulation of compositions of this invention and the benefits derived therefrom. They are illustrative of the invention and are not to be construed as limiting thereof.

# Example 1 Composition A was prepared by mixing the following components together in the order listed:

45	Component	grams	wt.% of active ingredient
	water	67.5	59.1
50	KTS (51.5%)	38.8	10.0
	Na₂CO₃	3.1	1.55
	NaHCO₃	2.5	1.25
55	Coconut fatty acid	3.6	1.8
	NaAE <sub>3</sub> S (27% active paste)	18.5	2.5
60	TKPP (60% solution)	46.0	13.8
	diethylene glycol mono n-butyl ether	20.0	10.0
65		200.0	100.0

In the table above, NaAE<sub>3</sub>S designates the sodium salt of the condensation product of 3 mols of ethylene oxide with coconut fatty alcohol. TKPP designates tetrapotassium pyrophosphate. KTS designates potassium toluene sulfonate. The coconut fatty acid was neutralized during the mixing process to form coconut soap. The pH of the composition was measured to be 9.5 when measured full strength and 9.3 when measured as a 1% aqueous solution.

This composition was tested for cleaning performance against 5 kinds of artificial soil designed to simulate in a reproducible manner a like number of natural soils found around a house:

- 1) Greasy/waxy soil found on kitchen floors: a mixture of cooking oil and floor-wax applied to vinyl-asbestos tiles; and aged.
- 2) Greasy soil found on kitchen walls: a mixture of cooking oil and humus applied to vinyl-asbestos tiles: baked: and aged.
- 3) Bathroom soil found in bathtubs: a mixture of skin oil, soap and humus applied to etched porcelain plates; three coats applied and baked; aged.
- 4) Bathroom soil found on walls above the tub or in a shower stalls or in toilet bowls: calcium stearate applied to smooth porcelain plates; baked.

All soils were pigmented with small amounts of carbon black to aid in the evaluation of cleaning performance. Cleaning tests were performed on a modified Gardner straight line tester (Gardner Lab Inc., Bethesda, Maryland, U.S.A.). In this machine, a rectangular sponge is moved back and forth across the test surface with constant, uniform pressure applied. The cleaning product was applied to the sponge, and a fixed number of strokes was made across the surface. The total number of strokes for each test was fixed at the point where the cleaning level of approximately 70 to 90% was visually estimated for the best composition in that particular test. Each product was replicated four times on different tiles.

Cleaning results were quantitively evaluated by using the L (lightness) values of a Hunter colorimeter (Hunter Associates Laboratory, Fairfax, Virginia, U.S.A.). Performance was measured as the percentage of soil removed. Quantitatively, where  $L_b$ =the L value of the substrate before soil was applied;  $L_s$ = the L value after soil was applied; and  $L_c$ = the L value after cleaning; the cleaning performance in % was calculated to be (100) ( $L_c$ - $L_b$ )/( $L_s$ - $L_b$ ).

In the performance tests described infra, liquid cleaning compositions were used full strength on both bathroom soils and on the greasy kitchen wall soil; while the liquid compositions were used in dilute form on both kitchen soils; making 5 tests in all. These practices simulated consumer practices in cleaning these surfaces, either full strength from the bottle or diluted in a scrub bucket. For test purposes, 2 grams of the liquid compositions were applied to each Gardner test sponge and used for full strength cleaning; while a mixture of 0.15 grams of the liquid composition with 9.85 grams of water was used for dilute cleaning. To simulate consumer use of dry abrasive cleanser, 2 grams of the composition plus 2 grams of water was applied to the sponge.

Cleaning performance was as follows:

10

15

Percentage (	of	soil	removed
--------------	----	------	---------

40	Circulate d	- -		Commercial products			
	Simulated Product Comp soil conc. A		Comp. A	Mr. Clean	Pine sol	Comet	
45	Kitchen floor	dilute	69%	71%	7%		
40	Kitchen wall	dilute	83%	74%	57%		
	Kitchen wall	full str.	90%	38%	81%	_	
50	Bathroom tub	full str.	85%	57%	52%	85	
	Shower wall	full str.	77%	25%	10%	40	

In the above comparison, Mr. Clean (TM Procter & Gamble Inc.) is a built liquid composition sold commercially for hard surface cleaning, containing sodium nitrilotriacetate and mixed diethanol amide/ethoxylated nonionic surfactant as principal cleaning ingredients; Pine Sol (TM American Cynamid Co.) is a liquid composition sold commercially for hard surface cleaning, containing pine oil, isopropanol and soap; and Comet (TM Procter & Gamble Inc.) is an abrasive cleanser sold for scouring tubs and sinks, containing finely divided silica as the scouring agent, and lesser amounts of anionic surfactant, chlorine bleach, and builder.

In the foregoing table, cleaning differences between products greater than about 3% are significant. Accordingly, Composition A, formulated according to this invention, was approximately equal to or was superior to each of these commercial products in every application. This same conclusion was also reached by a panel of graders who visually examined the tile surfaces after cleaning.

Note that it is appropriate to compare cleaning results for each type of soil as obtained for the 4

products tested (i.e. numbers within each single row of the table above). It is not appropriate to compare numbers within columns of the table, because the number of strokes on the test machine were different for each type of soil.

A second composition of this invention, B, was prepared that differed from A only in that 2% diethanolamine was used as buffer, replacing the mixture of 1.55% Na<sub>2</sub>CO<sub>3</sub> plus 1.25% NaHCO<sub>3</sub>, with a minor adjustment in the water content. The cleaning tests were repeated with approximately the same results

Composition C of this invention was like that of Composition A except that it contained 6% instead of 10% of diethylene glycol mono-n-butyl ether, with the difference made up by water.

10

55

65

Composition C was tested on the two bathroom soils in the manner hereinbefore described, and in the same series of tests, with the following results: 75% removal of simulated bathtub soil and 46% removal of simulated shower wall soil. It is apparent that the 6% solvent level, which is at the lower end of the formulation range of the compositions of this invention, while it reduces performance against both types of soil, is still well within the range of commercial products against bathtub soil and remains superior to all commercial products against shower wall soil.

Compositions A, B and C were homogeneous and were stable indefinitely at room temperature.

Example 2
The following homogeneous liquid compositions were similarly prepared, with all figures being opercent by weight, and the balance being water:

		D	E	F	G
	NaAE <sub>3</sub> S	2.5	0	2.5	2.5 wt.%
25	TKPP	13.8	13.8	10.0	13.8
	diethylene glycol mono n-butyl ether	10.0	10.0	10.0	5.0
30	coconut fatty acid	1.8	1.8	1.8	1.8
	Na₂CO₃	1.55	1.55	1.55	1.55
35	NaHCO <sub>3</sub>	1.25	1.25	1.25	1.25
	KTS	12.0	12.0	12.0	12.0

The above compositions were tested in the manner described in Example 1, with the following results:

40		<b>5</b>	Percentage of soil removed			
	soil	Product conc.	D	E	F	G
45	Kitchen floor	dilute	72	53	47	75 %
	Kitchen wall	dilute	56	41	49	55
	Kitchen wall	full str.	78	76	79	70
50	Bathroom tub	full str.	89	89	87	79
	Shower wall	full str.	79	79	51	69

Composition D is the only one of the foregoing that is according to this invention. It is clearly apparent from the above results that removal of surfactant or reduction of builder to a level outside the scope of this invention caused a significant reduction in cleaning when the compositions were used in dilute form on either simulated floor soil or wall soil; builder reduction diminished effectiveness against simulated shower wall soil as well. It is also clear that reduction of a solvent to a level outside the scope of this invention caused a significant reduction in cleaning when the compositions were used full strength on all three soils: simulated kitchen wall, bathroom tub and shower wall soils. These data demonstrate both the need and the effectiveness of concurrent high levels of both builder and solvent, in liquid compositions containing surfactant and other ingredients, to obtain the multiple cleaning objectives of this invention: a standard of accomplishment that has not been achieved heretofore.

Other compositions are prepared like Composition D except for the following differences:

Coconut fatty acid:

- i) omitted
- ii) increased to 4%
- iii) oleic acid substituted for coconut fatty acid

Substituted for TKPP:

- iv) ethane-1-hydroxy-1,1-diphosphonic acid, Na salt
- v) ethylene diphosphonic acid, Li salt
- 10 Substituted for NaAE<sub>3</sub>S:
  - vi) C<sub>16</sub> diethanolamide
  - vii) coconut monoethanolamide
  - viii) sodium coconut alkyl sulfate
  - ix) C<sub>14</sub> sodium paraffin sulfonate
- 15 x)  $C_{12}$  magnesium  $AE_6S$ 
  - xi) coconut dimethyl amine oxide
  - xii) sodium salt of N-lauryl-N,N-dimethyl ammonio-hydroxy-propane-sulfonic acid
  - xiii) 1.8% NaAE<sub>3</sub>S plus 0.7% C<sub>14</sub>AE<sub>6</sub> (linear alkyl ethoxylates containing 6 moieties of ethylene oxide per moiety of myristyl alcohol)

20

Substituted for carbonate/bicarbonate:

- xiv) sodium orthophosphate
- xv) sodium metasilicate
- 25 xvi) sodium tetraborate

The cleaning performance of the foregoing compositions is comparable to that of Composition D.

## Example 3

30 Compositions H and I were prepared according to this invention as follows:

		Н	1
<i>35</i>	Na-C <sub>11.8</sub> linear alkyl benzene sulfonate (LAS)	10.0	— wt.%
	· Na-AE₃S	_	2.3
40	TKPP	13.8	13.8
40	diethylene glycol mono-n-butyl ether	10.0	_
45	diethyl succinate		10.0
45	coconut fatty acid	1.8	0.6
	$Na_2CO_3$	1.6	1.6
50	NaHCO <sub>3</sub>	1.2	1.2
	KTS	12.0	
55	Na cumene sulfonate		7.0
30	Na₂SO₃/ammonia/opacifier/color	<del></del>	3.3
	water	bal.	bal.

Each of the above compositions was homogeneous and stable indefinitely at room temperature. A number of other compositions were prepared that were identical to Composition H except for differences in solvent. They too were homogeneous and stable indefinitely at room temperature. These solvents were: a mixture of 3% n-decane and 7% diethylene glycol mono-n-butyl ether (hereinafter referred to as DGBE); a mixture of 3% cyclohexane and 7% DGBE; a mixture of 3% xylene and 7% DGBE; a mixture of 5% xylene and 5% DGBE; a mixture of 2.2% diethyl benzene and 7.8% DGBE; 10% butyl acetate; 10% amyl acetate;

10% diethyl carbonate; 8% diethyl succinate; 7.5% methyl i-amyl ketone; 10% methyl i-amyl ketone; 10% ethylene glycol mono-n-butyl ether; 10% ethylene glycol mono-n-hexyl ether; 10% diethylene glycol mono-n-hexyl ether; 10% isopropylene glycol mono-butyl, ethyl and propyl ethers (Propasol BEP, TM Union Carbide Corp.); 6% pine oil and 4% isopropyl alcohol; 2% pine oil and 8% DGBE.

Compositions H and I were tested for cleaning performance on both bathroom soils in the manner described hereinbefore. Results were comparable to those of compositions A and D.

#### Example 4

10

The following composition was prepared; was homogeneous and stable at room temperature; and cleans well according to the tests described hereinbefore.

		J
15	NaLAS	8.0 wt.%
	Coconut fatty acid	1.4
20	TKPP	16.0
20	KTS	19.3
	diethanolamine	1.6
25	diethylene glycol mono-n-butyl ether	12.0
	water	bal.

#### Example 5

30

40

Certain pure solvents were screened for cleaning as described below. The Gardner test machine was used with simulated bathtub soil tiles and 2 grams of solvent per sponge. The data are consistent with the selection of solvent parameters that define the invention herein. The numbers which follow are the number of strokes required, as judged visually, to completely clean the tiles. Solvents meeting the criteria herein for principal solvent: trichloroethylene—4; xylene—5; hexane—5; chloroform—5; carbon tetrachloride—6. Solvents not meeting the criteria herein for principal solvent: methyl ethyl ketone—18; 1-butanol—20; diethylene glycol mono ethyl ether—35; ethanol—40; acetone—more than 45; methanol—more than 45.

# Example 6

The following compositions of this invention were prepared in greater quantity for the purpose of stability testing:

		K	L	Μ
45	NaLAS	10.0	4.0	— wt.%
	NaAE <sub>3</sub> S	_		2.5
50	Coconut fatty acid	1.8	1.8	1.2
50	TKPP	13.8	13.3	13.3
	KTS	12.0	7.0	12.0
55	Na <sub>2</sub> CO <sub>3</sub>	1.6	_	
	NaHCO <sub>3</sub>	1.2	_	_
60	diethanolamine		2.0	2.0
00	diethylene glycol mono-n-butyl ether	10.0	8.5	8.5
	perfume	_		0.75
6 <u>5</u>	water	bal.	bal.	bal.

Composition N was prepared identical to that of Composition K except that its solvent was 10% ethylene glycol mono-n-butyl ether. Compositions K and N were clear, homogeneous liquids and remained so after storage for 3 months at 4°, 21° and 49°C. Both fully recovered to their original homogeneous appearance after 3 cycles alternating between 24 hours at -18°C. and 72 hours at +10°C.

Composition O was prepared identical to that of Composition L except that the KTS level was 12%. Compositions L, M and O were tested using procedures and obtaining results the same as for Compositions K and N except that the storage tests at 4°, 21° and 49°C. were discontinued after 2 weeks, with no visible changes having occurred during that time.

Compositions containing higher or lower amounts of builder and/or solvent within the scope of this invention can be stabilized by adjusting levels of KTS and fatty acid within the ranges specified herein, according to principles known in the art. Diethanolamine is preferred to inorganic buffers from the standpoint of increasing stability under severe storage conditions.

#### Example 7

A series of compositions were prepared according to the method of Composition A for the purpose of comparing the inorganic builder of this invention with an aminopolycarboxylate builder, another common type of sequestering builder. Cleaning tests were run according to the methods of Example 1, using all compositions at full strength.

20		Р	Q	R
	Composition (wt.%) NaAE₃S	4	4	4
25	TKPP (mol. wt.=330)	13.8		<del></del>
	Na-nitrilotriacetate (mol. wt.=257)		10.75	13.8
	diethylene glycol mono n-butyl ether	10	10	10
30	coconut fatty acid	1.8	1.8	1.8
	Na <sub>2</sub> CO <sub>3</sub>	1.5	1.5	1.5
35	NaHCO₃	1.2	1.2	1.2
	KTS	12	12	12
40	Soil removal (%) Bathroom tub soil	89	66	68
	Shower wall soil	83	66	84

Composition Q, as compared with Composition P, represents equimolar substitution of trisodium nitrilotriacetate for TKPP, with all other ingredients remaining the same. Because sequestration is a chemical process and because costs are roughly comparable when examined in this way, this is a common, useful and valid type of comparison. It is apparent from the foregoing figures that the performance of Composition Q is seriously deficient in removal of both bathtub and shower soil.

Composition R, as compared with Composition P, represents equiponderant substitution of trisodium nitrilotriacetate for TKPP. Although Composition R cleans somewhat better than Composition Q as might be expected, its performance in removal of bathroom tub soil is still seriously deficient in comparison with that of Composition P.

#### Claims

55

60

- 1. A homogeneous aqueous liquid hard-surface cleaning detergent composition having a pH (1% aqueous solution) of from 8.5 to 11, comprising (all percentages being by weight of composition):
  - a) from 0.9% to 10% of a non-soap anionic, amphoteric, zwitterionic or nonionic surfactant;
  - b) from 0% to 5% soap;
  - c) an alkali metal polyphosphate or polyphosphonate sequestrant;
  - d) from 0% to 6% of an alkaline pH buffer;
- e) a Principal Solvent having a molar volume below 200 (cm³/g. mol) and solubility parameters at 25°C as follows: Polarity Parameter from 0 to 7.16 (J/cm³)<sup>1/2</sup> [=0 to 3.5 (cal/cm³)<sup>1/2</sup>] and Hydrogen Bonding Parameter from 0 to 12.28 (J/cm³)<sup>1/2</sup> [=0 to 6 (cal/cm³)<sup>1/2</sup>];
  - f) from 0% to 10% of an Auxiliary Solvent having a Polarity Parameter of 7.18 (J/cm³)1/2 [=3.51

 $(cal/cm^3)^{1/2}]$  or above and/or a Hydrogen Bonding Parameter of 12.30  $(J/cm^3)^{1/2}$  [=6.01  $(cal/cm^3)^{1/2}]$  or above:

- g) from 3% to 25% of a hydrotrope; and
- h) water;
- characterized in that sequestrant (c) is from 10.5% to 19% of the composition and Principal Solvent (e) is from 6% to 15% of the composition with the provisos that the sum of components (c) and (d) is not greater than 21% of the composition and the sum of components (e) and (f) is not greater than 22% of the composition.
- 2. A composition according to Claim 1 characterised in that element (a) the non-soap surfactant, is an anionic surfactant or is an alkyl ethanol amide; element (c), the sequestrant, is an alkali metal polyphosphate salt; element (d), the alkaline pH buffer, is from 0.5% to 6% by weight of the composition and is an alkali metal carbonate, bicarbonate, orthophosphate, borate, or silicate salt or is an ethanolamine; and element (e) the Principal Solvent, is from 8% to 12% by weight of the composition.
- 3. A composition according to Claim 2 characterized in that element (a), the non-soap surfactant, is from 2% to 7% by weight of the composition and is selected from C<sub>10</sub>—C<sub>18</sub> alkyl diethanol amide and the sodium salts of straight or branched chain C<sub>9-15</sub> alkyl benzene sulfonate, C<sub>10-18</sub> alkyl sulfate, and C<sub>10-18</sub> alkyl polyethoxy sulfate containing from 1 to 12 ethylene oxide moieties per fatty alcohol moiety; element (b) soap, is from 0.5% to 5% by weight of the composition; element (c), the sequestrant, is from 12% to 16% potassium tetraphosphate by weight of the composition; element (d), the alkaline pH buffer, is from 0.5% to 6% by weight of the composition and is diethanolamine; and element (g), the hydrotrope, is selected from the alkali metal salts of toluene sulfonate, xylene sulfonate and cumene sulfonate.
  - 4. A composition according to any of Claims 1 to 3 characterized in that element (e), the Principal Solvent, is selected from n-hexane, n-decane, cyclohexane, toluene, xylene, naphthalene, diethyl benzene, chlorobenzene, trichloroethylene, pine oil, alpha terpineol, d-limonene, orange terpene, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, isopropylene glycol mono ethyl ether, isopropylene glycol mono propyl ether, isopropylene glycol mono butyl ether, methyl cyclohexane, butyl acetate, amyl acetate, butyl butyrate, butyl lactate, diethyl carbonate, diethyl succinate, methyl i-amyl ketone, morpholine and anisole.
  - 5. A composition according to any of Claims 1—3 characterized in that element (e), the Principal Solvent, is selected from ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, isopropylene glycol mono ethyl ether, isopropylene glycol mono propyl ether, isopropylene glycol mono butyl ether, methyl cyclohexane, butyl acetate, amyl acetate, butyl butyrate, butyl lactate, diethyl carbonate, diethyl succinate, methyl i-amyl ketone, morpholine, and anisole; and wherein the Auxiliary Solvent is less than 2% by weight of the composition.
  - 6. A composition according to any of Claims 1 to 3 characterized in that element (e), the Principal Solvent, is selected from n-hexane, n-decane, chlorobenzene, trichloroethylene, pine oil, alpha terpineol, d-limonene, and orange terpene and wherein the Auxiliary Solvent is from 2% to 10% by weight of the composition and is selected from propylene carbonate, methyl ethyl ketone, acetone, ethylene glycol mono methyl ether, ethylene glycol mono ethyl ether, diethylene glycol mono methyl ether, diethylene glycol, glycerol, hexylene glycol, propylene glycol, ethylene glycol, 1-butanol, 1-propanol, and ethanol.
  - 7. A composition according to any of Claims 1 to 3 characterized in that element (e), the Principal Solvent, is selected from ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, isopropylene glycol mono ethyl ether, mixed isopropylene glycol mono-butyl, ethyl and propyl ethers, pine oil, alpha terpineol, orange terpene, methyl cyclohexane, toluene, xylene, butyl acetate and amyl acetate.
  - 8. A composition according to Claim 3 characterized in that element (e), the Principal Solvent, is from 10% to 12% by weight of the composition and is diethylene glycol mono-n-butyl ether.

## Patentansprüche

60

- 1. Homogenes, wäßriges, flüssiges Detergensgemisch zum Reinigen harter Oberflächen mit einem pH-Wert (in 1%iger wäßriger Lösung) von 8,5 bis 11, enthaltend (wobei sich alle Prozentsätze auf das Gewicht der Zusammensetzung beziehen):
  - a) 0.9 bis 10% eines anionischen, amphoteren, zwitterionischen oder nichtionischen oberflächenaktiven Nichtseifenmittels;
    - b) 0 bis 5% Seife;
    - c) ein Alkalimetallpolyphosphat oder -polyphosphonat als Sequestrierungsmittel;
    - d) 0 bis 6 % einer Puffersubstanz für einen alkalischen pH-Wert;
  - e) ein Hauptlösungsmittel mit einem Molvolumen unterhalb 200 (cm³/g Mol) und den folgenden Löslichkeitsparametern bei 25°C: Polaritätsparameter von 0 bis 7,16 (J/cm³)¹¹² [=0 bis 3,5 (cal/cm³)¹¹²] und Wasserstoffbindungsparameter von 0 bis 12,28 (J/cm³)¹¹² [=0 bis 6 (cal/cm³)¹²²];
  - f) 0 bis 10% eines Hilfslösungsmittels mit einem Polaritätsparameter von 7,18 (J/cm³)1/2 [=3,51

 $(cal/cm^3)^{1/2}$ ] oder darüber und/oder einem Wasserstoffbindungsparameter von 12,30 (J/cm³)<sup>1/2</sup> [=6,01 (cal/cm³)<sup>1/2</sup>] oder darüber;

- g) 3 bis 25% eines Hydrotrops; und
- h) wasser;

dadurch gekennzeichnet, daß das Sequentrierungsmittel (c) 10.5 bis 19% der Zusammensetzung ausmacht und das Hauptlösungsmittel (e) 6 bis 15% der Zusammensetzung ausmacht, mit den Maßgaben, daß die Summe der Bestandteile (c) und (d) nicht größer als 21% der Zusammensetzung ist und daß die Summe der Bestandteile (e) und (f) nicht größer als 22% der Zusammensetzung ist.

- 2. Zusammensetzung gemäß Anspruch 1, dadurch gekennzeichnet, daß das Element (a), das oberflächenaktive Nichtseifenmittel, ein anionisches oberflächenaktives Mittel oder ein Alkylethanolamid ist; das Element (c), das Sequestrierungsmittel, ein Alkalimetallpolyphosphatsalz ist; das Element (d), die Puffersubstanz für einen alkalischen pH-Wert, 0,5 bis 6 Gew.-% der Zusammensetzung ausmacht und ein Alkalimetallcarbonat, -bicarbonat, -orthophosphat, -borat oder -silikatsalz oder ein Ethanol-amin ist; und das Element (e), das Hauptlösungsmittel, 8 bis 12 Gew.-% der Zusammensetzung ausmacht.
  - 3. Zusammensetzung gemäß Anspruch 2, dadurch gekennzeichnet, daß das Element (a), das oberflächenaktive Nichtseifenmittel, 2 bis 7 Gew.-% der Zusammensetzung ausmacht und ausgewählt ist aus  $C_{10}$ — $C_{18}$ -Alkyldiethanolamid und den Natriumsalzen von geradkettigem oder verzweigtkettigem  $C_{9-15}$ -Alkylbenzolsulfonat,  $C_{10-18}$ -Alkylsulfat und  $C_{10-18}$ -Alkylpolyethoxysulfat mit 1 bis 12 Ethylenoxidanteilen pro Fettalkoholanteil; das Element (b), die Seife, 0,5 bis 5 Gew.-% der Zusammensetzung ausmacht; das Element (c), das Sequestrierungsmittel, 12 bis 16% Kaliumtetraphosphat, bezogen auf das Gewicht der Zusammensetzung, ist; das Element (d) die Puffersubstanz für einen alkalischen pH-Wert, 0,5 bis 6 Gew.-% der Zusammensetzung ausmacht und Diethanolamin ist; und das Element (g), das Hydrotrop, ausgewählt ist aus den Alkalimetallsalzen von Toluolsulfonat, Xylolsulfonat und Cumolsulfonat.
- 4. Zusammensetzung gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Element (e), das Hauptlösungsmittel, ausgewählt ist aus n-Hexan, n-Decan, Cyclohexan, Toluol, Xylol, Naphthalin, Diethylbenzol, Chlorbenzol, Trichlorethylen, Kienöl, alpha-Terpieol, d-Limonen, Orangenterpen, Ethylenglykol-mono-n-butylether, Ethylenglykol-mono-n-hexyl-ether, Diethylenglykol-mono-n-butylether, Diethylenglykol mono n hexylether, Isopropylenglykol monoether, Iso propylenglykol-monopropylether, Isopropylenglykol-monobutyl-ether, Methylcyclohexan, Butylacetat, Amylacetat, Butylbutyrat, Butyllactat, Diethlcarbonat, Diethylsuccinat, Methyl-i-amylketon, Morpholin und Anisol.
  - 5. Zusammensetzung gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Element (e), das Hauptlösungsmittel ausgewählt ist aus Ethylenglykol-mono-n-butylether, Ethylen-glykol-mono-n-hexylether, Diethylenglykol-mono-n-hexylether, Isopropylenglykol mono ethylether, Isopropylenglykol monopropylether, Isopropylenglykol monobutylether, Methyl-cyclohexan, Butylacetat, Amylacetat, Butylbutyrat, Butyllactat, Diethylcarbonat, Diethylsuccinat, Methyl-iamylketon, Morpholin und Anisol; und daß das Hilfslösungsmittel weniger als Gew.-% der Zusammensetzung ausmacht.
  - 6. Zusammensetzung gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Element (e), das Hauptlösungsmittel, ausgewählt ist aus n-Hexan, n-Decan, Chlorbenzol, Trichlorethylen, Kienöl, alpha-Terpineol, d-Limonen und Orangenterpen, und daß das Hilfslösungsmittel 2 bis 10 Gew.-% der Zusammensetzung ausmacht und ausgewählt ist aus Propylencarbonat, Methylethylketon, Aceton, Ethylenglykolmonomethylether, Ethylenglykol monoethylether, Diethylenglykol monoethylether, Diethylenglykol monoethylether, Benzylalkohol, Diethylenglykol, Glycerin, Hexylenglykol, Propylenglykol, Ethylenglykol, 1-Butanol, 1-Propanol und Ethanol.
  - 7. Zusammensetzung gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Element (e), das Hauptlösungsmittel, ausgewählt ist aus Ethylenglykol mono n butylether, Ethylenglykol mono n hexylether, Diethylenglykol mono n hexylether, lsopropylenglykol mono ethylether, gemischten Isopropylenglykol mono butyl , -ethyl- und -propylethern, Kienöl, alpha-Terpineol, Orangenterpen, Methylcyclohexan, Toluol, Xylol, Butylacetat und Amylacetat.
  - 8. Zusammensetzung gemäß Anspruch 3, dadurch gekennzeichnet, daß das Element (e), das Hauptlösungsmittel, 10 bis 12 Gew.-% der Zusammensetzung ausmacht und Diethylenglykol mono n butylether ist.

## Revendications

55

- 1. Composition détergente liquide aqueuse homogène pour le nettoyage des surfaces dures ayant un pH (solution aqueuse à 1%) de 8,5 à 11, comprenant (tous les pourcentages étant en poids de la composition):
  - a) de 0.9 à 10% d'un tensio-actif non saponacé amphotère, zwitterionique ou non ionique;
  - b) de 0 à 5% de savon;
  - c) un agent séguestrant à base de polyphosphate ou polyphosphonate de métal alcalin;
  - d) de 0% à 6% d'un tampon de pH alcalin;
  - e) un solvant principal ayant un volume molaire inférieure à 200 (cm³/g/mol) et des paramères de

solubilité à 25°C comme suit: Paramère de polarité de 0 à 7,6 (J/cm³) $^{1/2}$  [=0 à 3,5 (cal/cm³) $^{1/2}$ ] et un paramètre de liaisons hydrogène de 0 à 12,28 (J/cm³) $^{1/2}$  [=0 à 6 (cal/cm³) $^{1/2}$ ];

- f) de 0% à 10% d'un solvant auxiliaire ayant un paramètre de polarité de 7,18 (J/cm³)<sup>1/2</sup> [=3,51 (cal/cm³)<sup>1/2</sup>] ou plus et un paramètre de liaisons hydrogène de 12,30 (J/cm³)<sup>1/2</sup>]=6,01 (cal/cm³)<sup>1/2</sup> ou plus;
  - g) de 3% à 25% d'un hydrotrope; et

5

15

25

- h) de l'eau; caractérisée en ce que l'agent séquestrant (c) représente de 10,5% à 19% de la composition et que le solvant principal (e) représente de 6% à 15% de la composition à condition que la somme des composants (c) et (d) ne soit pas supérieure à 21% de la composition et que la somme des composants (e) et (j) ne soit pas supérieure à 22% de la composition.
- 2. Composition selon la revendication 1 caractérisé en ce que l'élément (a), le tensio-actif non saponacé est un tensio-actif anionique ou est un alkyl éthanol amide; l'élément (c), l'agent séquestrant, est un sel polyphosphate de métal alcalin; l'élément (d), le tampon de pH alcalin, représente de 0,5 à 6% en poids de la composition et est un carbonate, bicarbonate, orthophosphate, borate ou silicate de métal alcalin ou est une éthanolammine; et l'élément (e), le solvant principal, représente de 8 à 12% en poids de la composition.
- 3. Composition selon la revendication 2 caractérisée en ce que l'élément (a), le tensio-actif non saponacé, représente de 2% à 7% en poids de la composition et est choisi parmi les alkyl en  $C_{10}$ — $C_{18}$  diéthanol amides et les sels de sodium des alkyl en  $C_{9-15}$  benzène sulfonates à chaîne droite ou ramifiée, alkyl en  $C_{10-18}$  sulfates, et alkyl en  $C_{10-18}$  sulfates polyéthoxylés contenant de 1 à 12 fractions oxyde d'éthylène par fraction d'alcool gras; l'élément (b), le savon, représente de 0.5% à 5% en poids de la composition; l'élément (c), l'agent séquestrant, représente de 12% à 16% de tétraphosphate de potassium en poids de la composition; l'élément (d), le tampon de pH alcalin, représente de 0.5% à 6% en poids de la composition et est la diéthanolamine; et l'élément (g), l'hydrotrope, est choisi parmi les sels de métal alcalin du toluène sulfonate, du xylène sulfonate et du cumène sulfonate.
- 4. Composition selon l'une quelconque des revendications 1 à 3 caractérisée en ce que l'élément (e), le solvant principal, est choisi parmi le n-hexane, le n-décane, le cyclohexane, le toluène, le xylène, le naphtalène, le diéthylbenzène, le chlorobenzène, le trichloroéthylène, l'essence de pin, l'alpha terpinéol, le d-limonène, le terpène d'orange, le mono-n-butyl éther de l'éthylène glycol, le mono-n-hexyl éther de l'éthylène glycol, le mono-n-hexyl éther du diéthylène glycol, le mono-hexyl éther du diéthylène glycol, le mono-éthyl éther de l'isopropylène glycol, le mono-propyl éther de l'isopropylène glycol, le mono-butyl éther de l'isopropylène glycol, le méthyl cyclohexane, l'acétate de butyle, l'acétate d'amyle, le butyrate de butyle, le lactate de butyle, le carbonate de diéthyle, le succinate de diéthyle, la méthyl i-amyl cétone, la morpholine et l'anisole.
- 5. Composition selon l'une quelconque des revendications 1—3 caractérisée en ce que l'élément (e), le solvant principal, est choisi parmi le mono-n-butyl éther de l'éthylène glycol, le mono-n-hexyl éther de l'éthylène glycol, le mono-n-hexyl éther du diéthylène glycol, le mono-ethyl éther du diéthylène glycol, le mono-éthyl éther de l'isopropylène glycol, le mono-propyl éther de l'isopropyl glycol, le mono-butyl éther de l'isopropylglycol, le méthyl cyclohexane, l'acétate de butyle, l'acétate d'amyle, le butyrate de butyle, le lactate de butyle, le carbonate de diéthyle, le succinate de diéthyle, la méthyl i-amyl cétone, la morpholine et l'anisole; et dans laquelle le solvant auxiliaire représente moins de 2% en poids de la composition.
- 6. Composition selon l'une quelconque des revendications 1 à 3 caractérisée en ce que l'élément (e), le solvant principal, est choisi parmi le n-hexane, le n-décane, le chlorobenzène, le trichloroéthylène, l'essence de pin, l'alpha terpinéol, le d-limonène et le terpène d'orange et dans laquelle le solvant auxiliaire représente de 2% à 10% en poids de la composition et est choisi parmi le carbonate de propylène, la méthyl éthy cétone, l'acétone, le mono méthyl éther de l'éthylène glycol, le mono éthyl éther de l'éthylène glycol, le mono méthyl du diéthylène glycol, le mono éthyl éther du diéthylène glycol, l'alcool benzylique, le diéthylène glycol, le glycérol, l'hexylène glycol, le propylène glycol, l'éthylène glycol, le butanol-1, le propanol-1 et l'éthanol.
- 7. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce que l'élément (e), le solvant principal, est choisi parmi le mono-n-butyl éther de l'éthylène glycol, le mono-n-hexyl éther de l'éthylène glycol, le mono-n-butyl éther du diéthylène glycol, le mono-n-hexyl éther du diéthylène glycol, le mono éthyl éther de l'isopropylène glycol, les mono-butyl, éthyl et propyl éthers mixtes de l'isopropylène glycol, l'essence de pin, l'alpha terpinéol, le terpène d'orange, le méthyl cyclohexane, le toluène, le xylène, l'acétate de butyle et l'acétate d'amyle.
- 8. Une composition selon la revendication 3, caractérisée en ce que l'élément (e), le solvant principal, représente de 10 à 12% en poids de la composition et est le mono-n-butyl éther du diéthylène glycol.

60

55