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(54) Perfumed liquid abrasive cleaning composition.

(57) Problems of stability have bedeviled formulations of aqueous, liquid abrasive cleaning compositions comprising soluble abrasive particles. One factor which can influence the stability of aqueous compositions is the high level of electrolyte present in the compositions : ie. the soluble abrasive is typically immersed in an aqueous medium which is saturated with respect to that abrasive in solution. The electrolyte level varies with temperature and this can have detrimental effects on the product. We have now determined that these problems can be overcome by use of an essentially hydrophobic perfume composition as a stability enhancer in a pourable, aqueous, hard surface cleaning composition comprising water-soluble abrasive. Consequently, the present invention provides a pourable, aqueous, hard-surface cleaning composition comprising a water soluble abrasive, at least part of the abrasive being present as undissolved particles having a mean particle diameter of from 10 to 500 microns, further comprising and essentially hydrophobic perfume composition and a detergent, said composition remaining stable after storage at 37°C for twelve weeks or remaining stable after twelve temperature cycles from -5°C for eight hours to 25°C for sixteen hours.

EP 0 524 762 A2

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The invention relates to pourable, homogenous, abrasive, aqueous liquid detergent compositions containing a particulate abrasive which are suited to the cleaning of hard surfaces.

Liquid detergent compositions for cleaning hard surfaces have until recently been classified into two general types. The first are aqueous suspensions containing water-insoluble abrasive particles; such compositions can suffer from a stability problem and tend to be gritty in use, such that the surface being cleaned can become scratched. Also, difficulty can be experienced when rinsing with water a surface that has been cleaned with such a composition, as insoluble particles of the abrasive can be difficult to remove completely from the surface. The second are liquid detergent compositions, usually containing soap, non-ionics and alkyl benzene sulphonate, but with no abrasive particles.

Liquid detergent compositions of the latter type, although free from the possible problem of scratching in use, nevertheless suffer from a number of drawbacks which can limit their consumer acceptability. They can, for example, have poor cleaning performance on stubborn soil, especially in areas where the water is hard, due to the absence of an abrasive constituent. Moreover, the higher surfactant concentration necessary for in-use removal of grease and fatty solids can lead to excessive suds formation, which requires rinsing and wiping by the user. Although excessive suds production can be controlled to some extent by incorporation of a suds-regulating material such as solvents, hydrophobic silica and/or silicone or soap, this in itself can raise problems of poor product stability and homogeneity, and problems associated with deposition of insoluble residues on the items or surfaces being cleaned, leading to residual streaks and spots when dried.

A further type of liquid detergent composition was more recently proposed in EP-A-193375 (Unilever PLC, Unilever NV) which describes a pourable homogeneous abrasive aqueous detergent composition suitable for cleaning hard surfaces comprising water, 1.5 to 30wt detergent active compound, 6 to 45wt% water soluble salt at least 5wt% of which at 20°C comprises a solid phase in the form of undissolved particles having a mean particle diameter of 10 to 500μm, the salt having not more than a single hydrated species when present as a crystalline solid in water at a temperature of from 10 to 40°C in an amount above that required to form a saturated solution and a saturation solubility in water at 40°C which is less than ten times that at 10°C, the composition having a viscosity at 20°C of at least 6500 Pas at a shear rate of 3 x 10^{-5} sec^{-1} and not more than 10 Pas at a shear rate of 21 sec^{-1} EP-A-193375 thus describes a shear thinning liquid abrasive cleaner containing a water soluble abrasive in saturated solution. In use any surplus undissolved water-soluble salt abrasive remaining on the cleaned surface can readily be removed by rinsing with clean water in which it dissolves. The composition described in EP-A-193375 thus exhibits good rinsability.

Similar compositions comprising higher levels of water-soluble salt were known from US-A-4179414 (Mobil), but such products were thick pastes ie. were not creamy liquids. Such products are suitable for some uses but are generally unsuitable for convenient domestic use, eg. in situations where the product is dispensed from a plastic bottle via a nozzle. In these products stability of the paste is achieved by the interaction of sodium chloride with sodium hydrogen carbonate and certain diethanolamides.

Soluble abrasive products are also known from GB 1370377 (Procter & Gamble), disclosing non-aqueous detergent compositions having a scouring ability when concentrated and a dishwashing ability when diluted with water:

comprising a water miscible liquid medium (ie. glycerol), a solid particulate inorganic salt which is soluble in any added water (ie. NaCl), a solid anionic surfactant and a suspending agent (ie. starch). Other components, such as bacteriocides, tarnish inhibitors, enzymes, colourants and perfumes can be present.

US 3577347 (Procter & Gamble) lists many possible abrasives, of which a typical formulation includes sodium hydrogen carbonate, sodium cetyl benzene sulphonate, chlorinated trisodium phosphate and a perfume.

Other patents in the field include Colgate's US-4057506, which discloses the use of sodium tripolyphosphate as a particulate builder in a size range ineffective for scouring. The particles are in a colloidal size range below 1 micron in size and are held in suspension by an emulsifier component.

In hard surface cleaners containing particles, it is necessary to ensure that the particles remain in suspension in the composition. In one sub-class of compositions, the surfactant acts as a suspending agent, usually in combination with an electrolyte.

Surfactants employed as suspending agents in liquid abrasive cleaners have included, alkyl benzene sulphonates, alcohol ethoxylates, alkyl amido ethoxylates, fatty acid soaps and secondary alkyl sulphonates. Combinations of these surfactants, together with electrolytes are used to form a suspending system.

The fine structure of these suspending systems generally consists of spherical structures ranging from 0.05 to about 10 microns in diameter. These structures are believed to comprise concentric shells of alternating bilayers of surfactant molecules spaced apart by thin water layers. The suspending system is not the only structure which surfactants can form in the presence of water. The above-mentioned surfactants can also form micellar structures which are viscous but are not capable of suspending particles. In addition, compositions of surfactant and water may separate into two or more mixed phases with different physical properties.

It is essential, in liquid abrasive cleaners which employ surfactants as the suspending system, that the suspending system is stable over the range of temperatures encountered in use and sufficiently suspending to maintain the abrasive particles in suspension for the shelf life of the product. It is also necessary to consider the interactions of various other components in the composition with the suspending surfactants, particularly the electrolytes.

Despite the attention given to stability, problems of stability have bedeviled formulations of aqueous, liquid abrasive cleaning compositions comprising soluble abrasive particles. One factor which can influence the stability of aqueous compositions is the high level of electrolyte present in the compositions: ie. the soluble abrasive is typically immersed in an aqueous medium which is saturated with respect to that abrasive in solution. More particularly, as the composition of a saturated solution is highly dependent on the temperature of that solution, the electrolyte concentration will vary according to the storage and/or usage conditions of the products. These variations in the electrolyte concentration influence the suspending system and can under certain conditions destabilise the product.

The single liquid product known to be available in the marketplace comprises water soluble abrasive particles of with a volume weighted average particle size around 200 microns, but is known to phase-separate on storage into regions comprising higher and lower levels of abrasive particles as the particles settle out of the suspending medium. This leads to loss of cleaning efficiency and a failure to dispense the entire contents of a package.

We have now determined that these problems can be overcome by use of an essentially hydrophobic perfume composition as a stability enhancer in a pourable, aqueous, hard surface cleaning composition comprising water-soluble abrasive.

While perfume has previously been present in pourable hard surface cleaning compositions comprising a water-soluble abrasive the stability-improving advantage of this component has not previously been recognised.

Consequently, the present invention provides a pourable, aqueous, hard-surface cleaning composition comprising a water-soluble abrasive, at least part of the abrasive being present as undissolved particles having a mean particle diameter of from 10 to 500 microns, further comprising an essentially hydrophobic perfume composition and a detergent, said composition remaining stable after storage at 37°C for twelve weeks or remaining stable after twelve temperature cycles from -5°C for eight hours to 25°C for sixteen hours.

Typically, the level of perfume ranges from 0.1-10%wt on total composition.

Preferably the water soluble abrasive includes at least one compound selected from sodium hydrogen carbonate, potassium sulphate, sodium triphosphate hexahydrate and sodium tetraborate decahydrate.

More preferably, the water soluble abrasive is present at a level of 6-75wt% on total composition.

In typical embodiments of the invention there is provided a pourable, storage stable, homogeneous, abrasive, aqueous, detergent composition suitable for cleaning hard surfaces comprising, in addition to water:

i) at least 0.1%wt of an essentially hydrophobic, perfume composition;

ii) 1.5 to 30%wt of detergent active compound;

iii) a water soluble salt, in a quantity such that at 20°C at least 5% by weight of the overall composition comprises undissolved particles of said salt, said particles having a mean particle diameter of from 10 to 500 microns, said salt comprising not more than a single hydrated species when present as a crystalline solid in water at a temperature of from 10 to 40°C in an amount above that required to form a saturated solution, said salt having a saturation solubility in water at 40°C which is less than ten times that at 10°C, and said salt having a solubility in water of at least 1.2 g/l at 10°C,

Ideally, such compositions have a viscosity at 20°C of at least 6500 Pas at a shear rate of 3×10^{-5} sec^{-1} and not more than 10 Pas at a shear rate of 21 sec^{-1} as measured with a rotational viscometer.

Detergent active Compound

The composition according to the invention will comprise detergent actives which can be chosen from both anionic and non-ionic detergent actives.

Suitable anionic detergent active compounds are water-soluble salts of organic sulphuric reaction products having in the molecular structure an alkyl radical containing from 8 to 22 carbon atoms, and a radical chosen from sulphonic acid or sulphur acid ester radicals and mixtures thereof. Examples of anionic detergents are sodium and potassium alcohol sulphates, especially those obtained by sulphating the higher alcohols produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl benzene sulphonates such as those in which the alkyl group contains from 9 to 15 carbon atoms; sodium and potassium secondary alkanesulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulphates; sodium and potassium salts of sulphuric acid esters of the reaction product of one mole of a higher fatty alcohol and from 1 to 6 moles of ethylene oxide; sodium and potassium salts of alkyl phenol ethylene oxide ether sulphate with from 1 to 8 units of ethylene oxide molecule and in which the alkyl radicals contain from 4 to 14 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralised with sodium hydroxide where, for example, the fatty acids are derived from coconut oil and mixtures thereof.

The preferred water-soluble synthetic anionic detergent active compounds are the ammonium and substituted ammonium (such as mono, di and triethanolamine), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of higher alkyl benzene sulphonates and mixtures with olefinsulphonates and higher alkyl sulphates, and the higher fatty acid monoglyceride sulphates. The most preferred anionic detergent active compounds are higher alkyl aromatic sulphonates such as higher alkyl benzene sulphonates containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts of higher alkyl benzene sulphonates or of higher-alkyl toluene, xylene or phenol sulphonates, alkyl naphthalene sulphonates, ammonium diamyl naphthalene sulphonate, and sodium dinonyl naphthalene sulphonate.

The amount of synthetic anionic detergent active to be employed in the detergent composition of this invention will generally be from 1 to 25%, preferably from 2 to 20%, and most preferably from 2 to 15% by weight.

Suitable non-ionic detergent active compounds can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophillic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophillic or polyoxyalkylene radical 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 hydrophillic and hydrophobic elements. Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of polyoxyethylene radicals by weight and having a molecular weight of from 5,000 to 11,000; tertiary amine oxides of structure R_3N0, where one group R is an alkyl group of 8 to 18 carbon atoms and the others are each methyl, ethyl or hydroxyethyl groups, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure R_3P0, where one group R is an alkyl group of from 10 to 18 carbon atoms, and the others are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylphosphine oxide; and dialkyl sulphoxides of structure R_2S0 where the group R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans.

The amount of non-ionic detergent active to be employed in the detergent composition of the invention will generally be from 0.5 to 15%, preferably from 1 to 10%, and most preferably from 1 to 8% by weight.

Preferably, the compositions contain an amount of both the anionic and the non-ionic detergent active which is chosen so as to provide a structured liquid detergent composition, ie. one which is 'self' thickened without necessarily employing any thickening agent per se.

The weight ratio of anionic detergent to non-ionic detergent active may vary and will depend on their nature but is preferably in the range of from 1:9 to 9:1, ideally from 1:4 to 4:1.

According to a preferred embodiment illustrating this aspect of the invention, the detergent compositions will comprise from 2 to 10% by weight of a water-soluble, synthetic anionic sulphated or sulphonated detergent salt containing an alkyl radical having from 8 to 22 carbon atoms in the molecule, and from 0.5 to 8% by weight of an alkyleneoxylated non-ionic detergent derived from the condensation of an aliphatic alcohol having from 8 to 22 carbon atoms in the molecule with ethylene oxide, such that the condensate has from 2 to 15 moles of ethylene oxide per mole of aliphatic alcohol.

It is also possible opttionally to include amphoteric, cationic or zwitterionic detergent actives in the compositions according to the invention.

Suitable amphoteric detergent-active compounds that optionally can be employed are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 18 carbon atoms and an aliphatic radical substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane sulphonate and sodium N-2-hydroxydodecyl-N-methyltaurate.

Suitable cationic detergent-active compounds are quaternary ammonium salts having an aliphatic radical of from 8 to 18 carbon atoms, for instance cetyltrimethyl ammonium bromide.

Suitable zwitterionic detergent-active compounds that optionally can be employed are derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic radical of from 8 to 18 carbon atoms and an aliphatic radical substituted by an anionic water-solubilising group, for instance 3-

(N,N-dimethyl-N-hexadecylammonium)propane-1-sulphonate betaine, 3-(dodecylmethyl sulphonium) propane-1-sulphonate betaine and 3-(cetylmethylphosphonium) ethane sulphonate betaine.

Further examples of suitable detergent-active compounds are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents", Volume I by Schwartz and Perry and "Surface Active Agents and Detergents", Volume 11 by Schwartz, Perry and Berch.

The total amount of detergent active compound to be employed in the detergent composition of the invention will generally be from 1.5 to 30%, preferably from 2 to 15% by weight.

The Water-soluble Salt

The composition according to the invention preferably also comprises 6 to 75wt%, more preferably 6-45wt%, of at least one water-soluble salt. This salt will be present in the composition in an amount in excess of its saturation solubility in the solution, and will accordingly be present in both a dissolved and an undissolved state. The composition preferably therefore comprises a saturated aqueous solution of the salt, together with at least 5% by weight of the composition at 20°C in the form of a solid phase comprising particles or the salt having a volume distribution median particle diameter of from 10 to 500μm, preferably from 15μm to 300μm, more preferably from 20 to 100μm.

At higher levels of abrasive, especially at abrasive levels of from 45-75wt%, some additional attention must be given to the particle size.

Our published patent application EP 0193375, discloses how at abrasive levels in the range **45% up to 75%** a specific selection of a particle size range and size distribution within this range should be made. The teaching of the document is incorporated herein by reference.

The water-soluble salt, preferably an inorganic salt, normally possesses not more than a single hydrated species when present as a crystalline solid in water at a temperature of from 10° to 40°C in an amount in excess of that required to form a saturated solution. The saturation solubility of the salt in water at 40°C will be less than ten times, preferably less than eight times, and most preferably less than twice that at 10°C. This is to ensure that the characteristics of the product, in particular the size, shape and amount of crystalline abrasive particles, do not change significantly over the normal temperature range of use. Uniformity of performance is accordingly ensured. It is also apparent that the choice of a salt having the properties as defined herein will ensure that when the composition is self structured, that is the structure which provides the desired viscosity characteristics is derived from an appropriate choice of anionic and non-ionic detergent actives, it will remain stable without substantial change in viscosity.

Preferably, the water-soluble salt will have a Mohs hardness of less than 3, and a saturation solubility in water which at 10°C does not exceed 15% by weight.

The salt will also have a solubility in water of at least 1.2g/1, preferably at least 5g/1 at 10°C, to ensure that any surplus salt can readily be rinsed from a hard surface after cleaning with the composition. In this way, the surface can be free from residual spots or streaks.

The preferred salts are given overleaf together with data relevant to their saturation solubility in water and their hydrated species.

Salt Including hydrated species (10°C-40°C)	**Solubility 10°C**	**(% w/v) at 40°C**
sodium bicarbonate ($NaHCO_3$)	8	13
sodium triphosphate hexahydrate ($Na_5P_3O_{10}.6H_2O$)	14	14
sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$)	1.2	9.5

Mixtures of these salts can be employed.

Sodium bicarbonate is particularly preferred because:

i) it is cheap and readily available;

ii) it is non-toxic and does not harm the skin;

iii) its solubility in water does not vary much over the normal product storage temperature range of from O°C to 40°C, its solubility in g per 100ml at 10°C being 8 and at 40°C being 13;

iv) its saturation solubility in water at 10°C being about 8% by weight ensures that an excess of it will remain undissolved in the detergent composition to provide abrasive properties, whereas it is sufficiently soluble in water to dissolve when finally rinsing with water a hard surface that has been cleaned with the detergent composition;

v) it exists only in one crystalline form between 10°C and 40°C and does not exist as an hydrated form (ie. it does not contain water of crystallisation); its crystalline structure will therefore remain unchanged in the detergent composition during storage at normal temperatures;

vi) the crystalline form is sufficiently hard to exhibit good cleaning qualities, but since its hardness is a little less than that of calcite (ie. it has a hardness of less than 3 on the Moh scale), it is less likely to scratch a hard surface to the degree that can occur when using similar products containing a water-insoluble abrasive such as calcite, which has a Mohs hardness of 3.

No other abrasive material exhibits all these qualities.

Fine particles of sodium bicarbonate can be obtained by milling sodium bicarbonate as obtained in the marketplace or by purchase of particularly fine grade of bicarbonate such as that sold as 'extra-fine' by the BRUNNER-MOND company (previously ICI) of England. It is particularly preferable to use a salt being present as particles having a volume distribution diameter and span of less than 80 microns and between 1 and 3 respectively.

The total amount of the water-soluble salt present in the detergent composition, both in dissolved and undissolved form, should preferably be from 6 to 45%, more preferably from 10 to 40%, and ideally 15 to 40% by weight. At least 5% by weight of the water-soluble salt should be present in the composition, at normal storage or use temperatures of from 10°C to 40°C, in a solid, particulate form, having an average particulate size, and other characteristics, as herein defined.

In addition to sodium bicarbonate, potassium sulphate sodium tripolyphosphate hexahydrate and sodium tetraborate decahydrate, the composition according to the invention can also optionally comprise other water-soluble inorganic salts or organic salts of lithium, magnesium, sodium, potassium and calcium. Each of these optional salts can be present in the composition in an amount below or above its relevant saturation solubility. Mixtures of such salts can be employed.

Hydrophobic compound

The composition according to the invention will also comprise at least 0.1% by weight of an essentially hydrophobic compound or mixture thereof.

If the hydrophobic compound is a perfume, the perfume is preferably present in an amount of 0.1 to 2.0%

by weight of the composition. By "perfume" is meant any essentially water-insoluble fragrant substance or mixture of substances including natural, artificial and synthetic odoriferous substances. Typically, perfumes comprise complex mixtures of organic compounds such as odoriferous or fragrant essential oils, resinoids, resins, esters, ethers, aldehydes, alcohols, hydrocarbons, ketones, lactones, pyrrones and pyrroles. Examples of such perfume components are:

i) essential oils: pine, balsam, fir. citrus, evergreen, jasmine, lily, rose and ylang ylang;
ii) esters: phenoxyethyl isobutyrate, benzyl acetate, p-tertiary butyl cyclohexyl acetate, guaiacwoodacetate, linalyl acetate, dimethylbenzyl carbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethylmethylphenyl glycidate, allylcyclohexane propionate, styrallyl propionate and benzyl salicylate;
iii) ethers: benzylethyl ether;
iv) aldehydes: alkyl aldehydes of 8 to 18 carbon atoms, bourgeonal, citral, citronelal, citronellyl oxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal and lilial;
v) alcohols: anethol, citronellol, eugenol, geraniol, linalool, phenylethyl alcohol and terpineol;
vi) hydrocarbons: balsams and terpenes;
vii) ketones: ionones, alphaisomethyl ionone and methylcedryl ketone;
viii) lactones: gamma-alkyl lactone wherein the alkyl is of 8 to 14 carbon atoms;
ix) pyrrones: hydroxy-lower alkyl pyrrone wherein the alkyl is of 1 to 4 carbon atoms; and
x) pyrroles: benzopyrrole

Other perfumery materials which may also be employed, include pine oil, lemon oil, lime oil, orange oil, bergamot oil, sweet orange oil, petitgrain bigarade oil, rosemary oil, methyl anthranilate, dimethyl anthranilate, indole, jasmine oil, patchouly oil, vetiver bourbon oil, vanillin, ethyl vanillin, coumarin, 3-methyl nonan-3-yl-acetate, methyl ionone, synthetic lily of the valley oil, synthetic red rose oil, 3-methyl nonan-3-ol, alpha-amyl cinnamic aldehyde, methyl salicylate, amyl salicylate, lavandin, isobutyl heptenone, cedryl acetate, ethyl linalyl acetate, neryl acetate, nerol, d-limonene, cuminic aldehyde, linalyl propionate, nerolidyl acetate, nerolidyl formate, alpha-pinene, isobutyl linalool, methylnaphthylketone, linalyl isobutyrate, paracresyl caprylate, paracresyl phenolacetate, sandalwood oil, coriander oil, sassafras oil, cassia oil, angelica root oil, Peruvian balsam, clove oil, mace oil, menthol, oils of peppermint and spearmint, and almond oil.

Water

The composition according to the invention will also comprise water which will generally form from 25 to 92.4%, preferably from 40 to 80%, and ideally 50 to 70% by weight of the composition.

Optional Ingredients

The composition according to the invention can contain other ingredients which aid in their cleaning performance For example, the composition can contain detergent builders other than the special water-soluble salts, as defined herein, such as nitrilotriacetates, polycarboxylates, citrates, dicarboxylic acids, water-soluble phosphates especially polyphosphates, mixtures of ortho- and pyrophosphate, zeolites and mixtures thereof. Such builders can additionally function as abrasives if present in an amount in excess of their solubility in water as explained herein. In general, the builder, other than the special water-soluble salts when employed, preferably will form from 0.1 to 25% by weight of the composition.

Metal ion sequestrants such as ethylenediaminetetraacetates, amino-polyphosphonates (DEQUEST^R) and phosphates and a wide variety of other polyfunctional organic acids and salts, can also optionally be employed.

A further optional ingredient for compositions according to the invention is a suds regulating material, which can be employed in compositions according to the invention which have a tendency to produce excessive suds in use. One example of a suds regulating material is soap. Soaps are salts of fatty acids and include alkali metal soaps such as the sodium, potassium, ammonium and alkanol ammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 10 to about 20 carbon atoms. Particularly useful are the sodium and potassium and mono-, di- and triethanolamine salts of the mixtures of fatty acids derived from coconut oil and ground nut oil. When employed, the amount of soap can form at least 0.005%, preferably 0.5% to 2% by weight of the composition. A further example of a suds regulating material is an organic solvent, hydrophobic silica and a silicone oil or hydrocarbons.

The compositions according to the invention may optionally contain structuring agents to aid in providing appropriate rheological properties to maintain the undissolved salt or salts uniformly distributed in the composition and in enhancing their distribution and adherence of the composition to the hard surface to be cleaned. Preferred structuring agents include polysaccharides, such as sodium carboxymethyl cellulose and other chemically modified cellulose materials, xanthan gum and other non-flocculating structuring agents such as Biopolymer PS87 referred to in US Patent No. 4 329 448. Certain polymers such as a polymer of acrylic acid cross-linked with a poly functional agent, for example CARBOPOL^R, can also be used as structuring agents. The amount of such structuring agents, when employed, to be used in compositions according to the invention can be as little as 0.001%, preferably at least 0.01% by weight of the composition.

The composition according to the invention can also comprise at least partially esterified resin such as an at least partially esterified adduct of rosin and an unsaturated dicarboxylic acid or anhydride, or an at least partially esterified derivatives of co-polymerisation products of mono-unsaturated aliphatic, cycloaliphatic or aromatic monomers having no carboxy groups and unsaturated dicarboxylic acids or anhydrides thereof.

Typical examples of suitable copolymers of the latter type are copolymers of ethylene, styrene and vinylmethylether with maleic acid, fumaric acid, itaconic acid, citraconic acid and the like and the anhydrides thereof. Preferred are the styrene/maleic anhydride copolymers.

In general, the composition of the invention can optionally comprise from 0.005 to 20%, usually from 0.1 to 15% and preferably from 0.5 to 10% by weight of the at least partially esterified resin.

Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as pH regulants, colourants, optical brighteners, soil suspending agents, detersive enzymes, compatible bleaching agents, gel-control agents, freeze-thaw stabilisers, bactericides, preservatives, detergent hydrotropes and opacifiers.

The compositions according to the invention will not contain more than 10%, preferably not more than 5% by weight of a water-insoluble abrasive, such as calcite, in view of the tendency of such abrasives to leave a deposit on hard surfaces after cleaning, even when rinsed with water.

Ideally, compositions according to the invention are substantially free from water-insoluble abrasives.

Generally, the water and optional ingredients comprising other detergent adjuncts will form the balance of the composition, after accounting for the detergent active compound, the water soluble salt ingredients and the perfume.

pH

Compositions according to the invention are usually formulated in the alkaline pH range, and will generally have a pH of from 7 to 13, preferably about 7 to 11. In particular, if sodium bicarbonate is used as a soluble abrasive the pH should be in the range 8.0-9.5: outside of this range bicarbonate either decomposes to liberate carbon dioxide or is converted into the carbonate. Alkalising agents such as sodium hydroxyde and sodium carbonate can be used to adjust and buffer the pH as desired.

Suspending Properties

It is an important feature of the invention that the composition will be capable of stably suspending the undissolved particles of salt abrasive, so that the consumer does not need to agitate the composition, for example by shaking it, in order to re-suspend and re-distribute sedimented particles prior to use. For this purpose, the composition should have a viscosity at 20°C of at least 6500 Pas at a shear rate of 3×10^{-5} sec.$^{-1}$ to ensure that the particles of salt abrasive do not sediment on standing at 20°C by more than 1 cm in one month.

While it is necessary to ensure that the composition according to the invention has a viscosity which is high enough to prevent any substantial settlement of the undissolved particles of salt abrasive during storage, it should remain fluid, so that it can readily be poured from a bottle or other container when required for use. For this purpose, the composition should have a viscosity at 20°C, measured using a rotational viscometer which does not exceed 10 Pas at a shear rate of 21 sec.-1. Preferably, the viscosity at 20°C is no greater than 5 Pas at a shear rate of 21 sec^{-1}.

Suitable rheological conditions to suit these criteria can be provided by judicial choice of anionic and nonionic detergent to provide a structured liquid having the requisite suspending properties, and/or by use of an appropriate amount of an alternative structuring agent such as is described herein.

Preferred Embodiment

Particularly preferred embodiments of the present invention provide a pourable, aqueous, hard-surface cleaning composition having a viscosity at 20°C of at least 6500 Pas at a shear rate of 3×10^{-5} sec^{-1} and not more than 10 Pas at a shear rate of 21 sec^{-1} as measured with a rotational viscometer, said composition comprising:

i) 0.1-2wt% of an essentially hydrophobic, perfume composition,

ii) 4-20wt% of detergent active component, comprising a mixture of non-ionic and anionic surfactants in a ratio of 1:10 to 10:1, and,

iii) sodium bicarbonate, in a quantity such that at 20°C at least 5% by weight of the overall composition comprises undissolved particles of said salt, said particles having a mean particle diameter of from 10 to 500 microns.

Process for Preparation of Compositions

Since the compositions according to the invention are in liquid form, they can be prepared simply by blending the essential and optional ingredients in water.

Packaging and Use of the Compositions

The compositions according to the invention are pourable liquids that are preferably contained in a closable container for convenience of storage, transport and sale, without spillage.

The compositions are particularly suited to the cleaning of soiled hard surfaces, such as those to be found in the domestic kitchen and bathroom. The compositions can be used neat, that is without dilution, or they can first be diluted as required with water before application to a solid surface using, for example, a cloth, brush or sponge for ease of application. Following use, any surplus undissolved water-soluble salt abrasive remaining on the surface can readily be removed by rinsing with clean water in which it dissolves.

Surfaces cleaned in this way with compositions of the invention show less of a tendency to residual streaking or spotting than surface cleaned with corresponding products containing water-insoluble abrasives such as calcite.

EXAMPLES

The invention is illustrated by the following examples.

In the examples, the compounds listed below are identified by their trademarks.

DOBS 102	Linear alkyl benzene sulphonate: obtained as alkylate ex. Shell and sulphonated in house.
DOBS 113	Linear alkyl benzene sulphonate: obtained as alkylate ex. Shell and sulphonated in house.
PETRELAB 550	Linear alkyl benzene sulphonate: obtained as alkylate ex PETRESA and sulphonated in house.
DOBANOL 23 (6.5 EO)	Alcohol ethoxylate ex. Shell: used as received.
PRIFAC 7901	Fatty acid ex. Unichema: used as sodium salt following neutralisation with NaOH.
LEMONSTAR	A proprietary perfume composition obtained from the Firmenich company (CH).
BUPPA	A proprietary perfume composition obtained from the Firmenich company (CH).
Dowanol PnB	n-butoxy propanol ex. Dow.
Isopar L	iso-paraffin ex. Exxon.

The sodium hydrogen carbonate was extra-fine grade sodium hydrogen carbonate ex. Brunner Mond.

The formulations employed for the examples and for comparative examples are given in table 1 below. These compositions were suitable for cleaning hard surfaces such as sinks, worktops, baths and floors.

Table 1

EXAMPLES	1	2	3	4	5	A	B	C	D	E
DOBS 102 (Na salt)	5	-	6.2	3.5	-	5	5	5	5	-
DOBS 113 (Na salt)	-	5	-	-	-	-	-	-	-	-
DOBANOL 23 (6.5 EO)	2.5	2.5	3.1	1.7	3.08	2.5	2.5	2.5	2.5	3.08
PRIFAC 7901 (Na salt)	0.8	0.8	1.0	0.6	1.03	0.8	0.8	0.8	0.8	1.03
$NaHCO_3$	35	25	20	55	37.5	35	35	35	35	37.5
Petrolab 550 (Na Salt)	-	-	-	-	6.16	-	-	-	-	6.16
Lemonstar	0.7	0.7	0.9	0.5	-	-	-	-	-	-
Buppa	-	-	-	-	0.5	-	-	-	-	-
Isopar L	-	-	-	-	-	0.7	-	-	-	-
Dowanol PnB	-	-	-	-	-	-	0.7	-	-	-
Ethanol	-	-	-	-	-	-	-	0.7	-	-
NaOH to pH 9.0, water to 100%	-	-	-	-	-	-	-	-	-	-
Stability	S	S	S	S	S	F	F	F	U	F

Stability is expressed as:

S: Abrasive did not sediment either after storage at 37°C after twelve weeks or after twelve temperature cycles from -5°C for eight hours to 25°C for sixteen hours.

F: Abrasive sedimented during twelve temperature cycles from -5°C for eight hours to 25°C for sixteen hours.

U: Composition was unstable on storage at 37°C for twelve weeks.

Examples 1-4 are examples of the present invention and it can be seen that the products remained stable under the defined storage conditions. Examples A-D are comparative examples which illustrate that the compositions are unstable in the absence of the perfume and only partially stable in the presence of organic solvents other than perfumes. In particular, compositions A-C were unstable in conditions which approximated those which might be encountered during the winter months in a temperate climatic zone.

While we would not wish to be found by this theory, it is believed that the presence of the hydrophobic compound aids in the formation of lamellar phase spherulites by associating with the surfactant headgroup region and thus increases the lamellar phase volume.

Claims

1. Use of an essentially hydrophobic perfume composition as a stability enhancer in a pourable, aqueous, hard surface cleaning composition comprising water-soluble abrasive.

2. Use of an essentially hydrophobic perfume composition according to claim 1, wherein the level of perfume ranges from 0.1-10%wt on total composition.

3. Use of an essentially hydrophobic perfume composition according to claim 1 or 2, wherein the water soluble abrasive includes at least one compound selected from sodium hydrogen carbonate, potassium sulphate, sodium triphosphate hexahydrate and sodium tetraborate decahydrate.

4. Use of an essentially hydrophobic perfume composition according to claim 1, 2 or 3 wherein the water soluble abrasive is present at a level of 6-75wt% on total composition.

5. Use according to claim 4 wherein the water soluble abrasive is present at a level of 6-45wt% on total composition.

6. Pourable, aqueous, hard-surface cleaning composition comprising a water soluble abrasive, at least part of the abrasive being present as undissolved particles having a mean particle diameter of from 10 to 500 microns, further comprising and essentially hydrophobic perfume composition and a detergent, said composition remaining stable after storage at 37°C for twelve weeks or remaining stable after twelve temperature cycles from -5°C for eight hours to 25°C for sixteen hours.

7. Composition according to claim 6 comprising:
   i) at least 0.1%wt of an essentially hydrophobic, perfume composition;
   ii) 1.5 to 30%wt of detergent active component, and;
   iii) a water soluble salt, in a quantity such that at 20°C at least 5% by weight of the overall composition comprises undissolved particles of said salt, said particles having a mean particle diameter of from 10 to 500 microns, said salt comprising not more than a single hydrated species when present as a crystalline solid in water at a temperature of from 10 to 40°C in an amount above that required to form a saturated solution, said salt having a saturation solubility in water at 40°C which is less than ten times that at 10°C, and said salt having a solubility in water of at least 1.2 g/l at 10°C.

8. Composition according to claim 7 having a viscosity at 20°C of at least 6500 Pas at a shear rate of 3 x 10-5 sec-1 and not more than 10 Pas at a shear rate of 21 sec-1 as measured with a rotational viscometer.

9. Composition according to claim 7 comprising 6-45wt% of the water soluble salt (iii).

10. Composition according to claim 7 comprising 45-75wt% of the water soluble salt (iii) said salt being present as particles having a volume distribution diameter and span of less than 80 microns and between 1 and 3 respectively.

11. Composition according to any one of claims 6-10 wherein the salt is selected from the group comprising sodium bicarbonate, sodium triphosphate hexahydrate, sodium tetraborate decahydrate and mixtures thereof.

12. Composition according to claim 11 wherein the salt is sodium bicarbonate.

13. Pourable, aqueous, hard-surface cleaning composition having a viscosity at 20°C of at least 6500 Pas at a shear rate of 3×10^{-5} sec^{-1} and not more than 10 Pas at a shear rate of 21 sec^{-1} as measured with a rotational viscometer, said composition comprising:

i) 0.1-2wt% of an essentially hydrophobic, perfume composition,

ii) 4-20wt% of detergent active component, comprising a mixture of non-ionic and anionic surfactants in a ratio of 1:10 to 10:1, and,

iii) sodium bicarbonate, in a quantity such that at 20°C at least 5% by weight of the overall composition comprises undissolved particles of said salt, said particles having a mean particle diameter of from 10 to 500 microns.