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(71) Applicant *(for all designated States except MN, US)*: **RECKITT BENCKISER N.V.** [NL/NL]; Kantoorgebouw De Appelaer, De Fruittuinen 2-12, NL-2132 NZ Hoofddorp (NL).

(71) Applicant *(for MN only)*: **RECKITT BENCKISER (UK) LIMITED** [GB/GB]; 103-105 Bath Road, Slough, Berkshire SL1 3UH (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **DE DOMINICIS, Mattia** [IT/IT]; Reckitt Benckiser Italia, Piazza S. Nicolo 12/3, I-30034 Mira VE (IT).

(74) Agents: BROWN, Andrew, Stephen et al.; Reckitt Benckiser plc, Group Patents Department, Dansom Lane, Hull HU8 7DS (GB).

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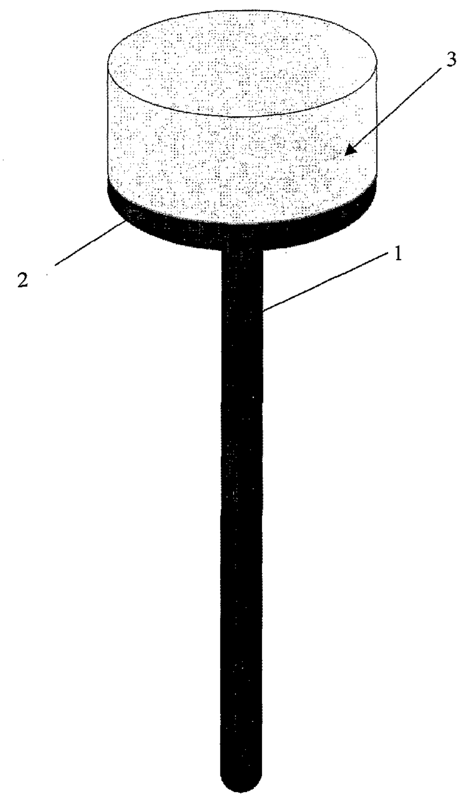
(54) Title: METHOD OF CLEANING



(57) Abstract: The invention relates to method of treating fabric by the production of a stable foam from a cleaning formulation and applying the stable foam to the fabric, the invention includes the formulation itself comprising a source of hydrogen peroxide as sodium percarbonate and at least one other surfactant.

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METHOD OF CLEANING

The invention relates to method of treating soft surfaces by the production of a stable foam from a solution of a cleaning formulation and applying the stable foam to the fabric, the invention includes the cleaning formulation itself comprising a source of hydrogen peroxide, such as sodium percarbonate, and at least one surfactant. The invention includes a device for a preparation of the stable foam.

We have found a new method of removing stains from soft surfaces by the production of a stable foam, which is formed from a cleaning formulation, as described herein. The stable foam can be used for direct treatment of stains on soft surfaces (fabric or carpet) and it is prepared by mixing a solution of a cleaning formulation, preferably in combination with aerating, for, preferably, less than 5, 4, 3, 2 minutes: preferably the foam is formed quickly, in less than 1 minute, between 5 and 50, 10 and 40 seconds from mixing with water. Preferably the cleaning formulation is a solid, such as a granular, compacted or powder composition, ideally the cleaning formulation is granular or powder, to aid dissolution in water. Preferably warm water is used (greater than 25, 30, 40 or 50°C, ideally less than 80, 70, 60, 50°C).

We present as a feature of the invention a method of cleaning stains on a soft surface the method comprising mixing (preferably dissolving) a solid, preferably a powder, cleaning formulation in water, the formulation comprising a source of active oxygen and at least one surfactant with water to form a stable foam and applying the foam directly onto the stained soft surface.

A further feature of the invention includes a device for the aeration of aqueous surfactant mixtures comprising a cellular plastic attached to a rigid support surface the opposition face of the rigid support surface being attached to a handle.

A further feature of the invention includes a kit for treating stain on soft surfaces comprising a solid, preferably a powder, stain cleaning composition comprising a source of active oxygen and at least one surfactant and a device for the mixing/ aerating of the cleaning composition to form a stable foam for application onto the stain.

Further optional subsequent steps include one or more of the following;

a) rubbing the stained soft surface;
b) cleaning the fabric in a fabric washing machine, with or without the addition of a fabric detergent;
c) rinsing with water the stable foam formulation from the soft surface.

The time period between applying the stable foam and any of the subsequent steps is at least 10, 20, 30, 40, 50, 60 seconds, ideally more than 1, 2, or 3 minutes, advisably the stable foam is not left for more than 10, 9, 8, 7, 6, 5, or 4 minutes.

By the use of the term stable we mean that the foam retains at least 80%, 90% or 95% of its volume for 2 minutes after its formation. Ideally the foam is prepared by dissolving 15 grams of solid composition into 100 ml of water at 40°C.

The stable foam may be prepared by any suitable mixing device or aeration device to incorporate air into the cleaning formulation solution.

The ?????? device offers particular advantages in ensuring that all of the solid composition is dissolved prior to application. This ???? for preventing fibre or colour damage on the soft surface since undissolved solids found on the fibre can provide for localised ????? due largely to the high concentration of active oxygen. By simply applying the stable foam on the fabric such damage is virtually eliminated as undissolved solid remains at the bottle of the water container

A cleaning solution containing a foaming surfactant is necessary for preparing the stable foam. In addition the inclusion of the cleaning formulation of a source of active oxygen provides for oxygen to be evolved during dissolution further providing a rapid development of the stable foam. In addition to the device, a container is also ideally required where the stable foam is prepared.

As a preferred feature of the invention the stable foam is prepared by the use of cellular plastic. Cellular plastics are those with a density of between 1 and 500 kg/m^3 preferably between 20 and 80 kg/m^3 and with an average pore diameter of at least 0.1 mm, preferably at least 0.4 mm. Ideally, the cellular plastic has a porosity of >50%, >60%, >70% or >80%.

The "porosity" according to the embodiment is obtained by measuring with a dry automatic densimeter an apparent volume and a true volume of the cellular pastic material, and calculated in accordance with the following equation.

Porosity %=(apparent volume-true volume)/apparent volumex100

The "average pore diameter" is a value measured in accordance with ASTM (Designation: D4404-84) and is specifically a value determined by the measurement of the diameter of pores in accordance with a mercury penetration process using a mercury porosimeter manufactured by Porous Material, Inc.

Suitable cellular plastics are those readily available for example from Euro foam, Miarka and Menshen and are made by any table water-insoluble plastic such as cellulose, polyurethane, polyester, polyether, or blends thereof.

Preferably the cellular plastic is attached to a handle so that the user does not need to get their hands wet. The device comprising the cellular plastic is plunged into the cleaning formulation containing solution and pressed several times such that the liquid is aerated to form the stable foam when the formulation is squeezed through the cellular plastic.

The device can be moved up and down pushing it against the bottom of a suitable container, until the cleaning formulation is transformed into the stable foam. The time necessary to create the foam with a suitable cellular plastic is quite low, between 10 and 60 seconds, typically below 2 minutes. The solution is pumped by each up and down movement through the pores of the cellular plastic to form the stable foam.

The liquid excess can be squeezed out from the cellular plastic component. The cellular plastic can be then dipped into the foam and applied onto the surface to be treated. The device can also be used to rub the surface with the cellular plastic component. During the rubbing action the cleaning foam can more easily penetrate the stain that can in addition be adsorbed by the cellular plastic. To complete the cleaning, a rinsing step might be necessary or eventually in the case of fabric, a normal wash can be done in a fabric washing machine.

Referring to figure 1 the device consists of at least two components, a handle 2 and cellular plastic 1, attached to the handle by a glue or a heat seal.

The handle (1) can be formed for example by one piece or two identical stick parts attached together through a screwing system. Each stick has a diameter from 1 mm to 6 cm, preferably from 3 mm to 12 mm and it may have a cavity running through the centre to reduce weight and material costs. The wall thickness of the handle (1) is from 0.1 mm up to 1 mm, preferably between 0.1 mm to 0.5 mm. The handle length may range from 1 cm up to 25 cm, preferably from 3 cm to 15 cm. The handle can be made of wood, metal or plastic. Preferred is a plastic material and more preferred plastic materials are polyethylene, polypropylene, polystyrene, or PET.

The handle is attached to a support (2) that is a disk with a diameter from 1 cm to 30 cm, preferably from 3 cm to 10 cm. The thickness can range from 0.1 mm up to 12 cm, preferably from 0.5 to 10 mm. The support (2) can be made of wood, metal or plastic. Preferred is plastic material and more preferred are polyethylene, polypropylene, polystyrene, or PET.

The cellular plastic (3) can be any shape but is preferably cylindrical shape. The diameter can range from 1 cm to 20 cm, preferably from 3 cm to 10 cm. The height can range from 0.1 mm up to 50 mm, preferably from 1 to 10 mm. The cellular plastic can be made of synthetic materials as polyurethane, polyester, polyether, or a blend thereof or natural cellulose.

The support (2) can be attached to the handle (1) by heat sealing, with a glue or with any screw system type. The cellular plastic(3) is attached to the support (2) by heat sealing or with a glue.

Preferably the cleaning formulation contains oleoyl sarcosinate (preferably as a sodium salt), a source of active oxygen, such as sodium percarbonate, and preferably at least one other surfactant.

We have found better performance is observed with the use of oleoyl sarcosinate, especially where the composition is applied directly onto the stain. The above surfactant types can be used in combination with other surfactants, such as alcohol ethoxylates and alkyl sulphates. A combination of alkyl naphthalene sulfonates and oleoyl sarcosinates provide improved stain removal efficacy for laundry detergent products. The alkyl naphthalene sulfonates and oleoyl sarcosinate surfactant combination of the present invention can be also used in combination with a source of active oxygen, such as sodium percarbonate, and bleach activators, such as TAED. Other ingredients that can be used include polymers, chelating agents, fillers, solvents, enzymes, fragrances and other minor components such as preservatives, dyes, thickeners and antifoaming agents.

Actives present in the detergent formulations of this invention include an one or more of the following:

a) Anionic and/or nonionic surfactant, preferably an oleoyl sarcosinate and/or an alkyl naphthalene sulfonate and/or an alkyl sulphate each at an overall level of 0.1 to 30%wt, preferably 0.5 to 20%wt, and ideally 1 to 10%wt.
b) Source of active oxygen, such as sodium percarbonate, preferably at a range of 0.1 to 80%wt, preferably from 10 to 70%wt, and ideally 30 to 60%wt.
c) Builder, such as polymers or chelating agents, preferably at a range of 0.1 to 80%wt, preferably from 1 to 60%wt, and ideally from 10 to 50%wt.
d) Bleach activator, such as TAED, preferably at a level of 0.1 to 8%wt, preferably from 0.2 to 7%wt.
e) Superwetting agent, preferably at a level from 0.01 to 10%wt.
f) Filler, such as sodium sulfate, preferably to 100% formula composition.

Ideally the soft surface is a fabric, ideally clothing. The composition is particularly effective on coloured fabric, especially cotton, providing for ? colour safe bleaching composition.

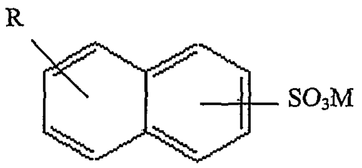
Alkyl Sulphate

Alkyl sulphate surfactants for use herein are those according to the formula R_2SO_4M wherein R_2 represents a saturated or unsaturated alkyl group containing from 9 to 30 carbon atoms, preferably from 9 to 18 carbon atoms, more preferably from 9 to 14, even more preferably from 9 to 12 and most preferably 10. The alkyl group can be in straight or branched configuration, and preferably in straight configuration. M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium) or ammonium or substituted ammonium cations. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethylammonium and quaternary ammonium cations, such as tetramethylammonium, dimethyl piperidinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof.

Suitable examples are sodium, potassium, ammonium nonyl sulphate, decyl sulphate, dodecyl sulphate and/or octyl decyl sulphate. For example, sodium decyl sulphate is commercially available from ALLBRIGHT & WILLSON under the name EMPICOL 0137®.

Alkyl naphthalene sulfonate:

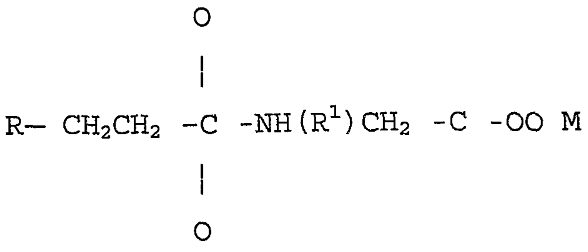
Alkyl naphthalene sulfonate anionic surfactants are described in the formula below:



wherein R is a straight chain or branched alkyl chain having from about 1 to about 25 carbon atoms, saturated or unsaturated, and the longest linear portion of the alkyl chain is 15 carbon atoms or less on the average, M is a cation capable of washing the compound more water soluble than the free acid especially preferred is an alkali metal (such as sodium or magnesium), or ammonium or substituted ammonium preferred cation.

Oleoyl sarcosinate

Oleoyl sarcosinates are described below:



$$R-CH_2CH_2-\overset{\overset{O}{|}}{\underset{\underset{O}{|}}{C}}-NH(R^1)CH_2-C-OO\ M$$

wherein R and R^1 is a straight chain or branched alkyl chain having from 1 to about 30 carbon atoms, saturated or unsaturated, and the longest average linear portion of the alkyl chain is 15 carbon atoms or less, M is a cation capable of making the compound more water soluble especially than the free acid, especially preferred is an alkali metal (such as sodium, potassium or magnesium), or ammonium or substituted ammonium cation, NRx and x is from 0 to about 4.

Additional surfactants:

Preferred total level of surfactant is in the range from 0.01 to 50% wt, ideally 0.1 to 30% wt and preferably 0.5 to 10% wt. Additional nonionic and anionic surfactants can be used.

The nonionic surfactant is preferably a surfactant having a formula RO(CH2CH2O)nH wherein R is a mixture of linear, even carbon-number hydrocarbon chains ranging from C12H25 to C16H33 and n represents the number of repeating units and is a number of from about 1 to about 12. Examples of other non-ionic surfactants include higher aliphatic primary alcohol containing about twelve to about 16 carbon atoms which are condensed with about three to thirteen moles of ethylene oxide.

Other examples of nonionic surfactants include primary alcohol ethoxylates (available under the Neodol tradename from Shell Co.), such as C11 alkanol condensed with 9 moles of ethylene oxide (Neodol 1-9), C12-13 alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C12-13 alkanol with 9 moles of ethylene oxide (Neodol 23-9), C12-15 alkanol condensed with 7 or 3 moles ethylene oxide (Neodol 25-7 or Neodol 25-3), C14-15 alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), C9-11 linear ethoxylated alcohol, averaging 2.5 moles of ethylene oxide per mole of alcohol (Neodol 91-2.5), and the like.

Other examples of nonionic surfactants suitable for use in the present invention include ethylene oxide condensate products of secondary aliphatic alcohols containing 11 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available non-ionic detergents of the foregoing type are C11-15 secondary alkanol condensed with either 9 moles of ethylene oxide (Tergitol 15-S-9) or 12 moles of ethylene oxide (Tergitol 15-S-12) marketed by Union Carbide, a subsidiary of Dow Chemical.

Octylphenoxy polyethoxyethanol type nonionic surfactants, for example, Triton X-100, as well as amine oxides can also be used as a nonionic surfactant in the present invention.

Other examples of linear primary alcohol ethoxylates are available under the Tomadol tradename such as, for example, Tomadol 1-7, a C11 linear primary alcohol ethoxylate with 7 moles EO; Tomadol 25-7, a C12-C15 linear primary alcohol ethoxylate with 7 moles EO; Tomadol 45-7,a C14-C15 linear primary alcohol ethoxylate with 7 moles EO; and Tomadol 91-6, a C9-C11 linear alcohol ethoxylate with 6 moles EO.

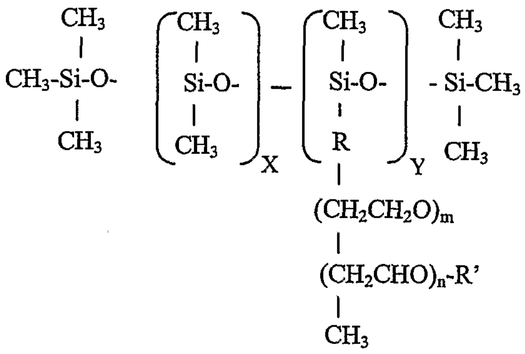
Other nonionic surfactants are amine oxides, alkyl amide oxide surfactants.

Preferred anionic surfactants are frequently provided as alkali metal salts, ammonium salts, amine salts, aminoalcohol salts or magnesium salts. Contemplated as useful are one or more sulfate or sulfonate compounds including: alkyl benzene sulfates, alkyl sulfates, alkyl ether sulfates, alkylamidoether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates, alkylsulfonates, alkylamide sulfonates, alkylarylsulfonates, olefinsulfonates, paraffin sulfonates, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide sulfosuccinates, alkyl sulfosuccinamate, alkyl sulfoacetates, alkyl phosphates, alkyl ether phosphates, acyl sarcosinates, acyl isethionates, and N-acyl taurates. Generally, the alkyl or acyl radical in these various compounds comprise a carbon chain containing 12 to 20 carbon atoms.

Superwetting agents:

A super wetting agent is capable of reducing the surface tension in water at values below 25 mN/m, in the range between 18 and 25 mN/m at concentrations of 0.0001-1%wt, preferably between 0.001 and 0.1%wt.

Preferred levels in the cleaning composition are between 0.01 and 10%wt. Examples of super wetting agents of this invention are silicone glycol copolymers and flurosurfactants. The silicone glycol copolymers are described by the following formula:



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\left(\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\right)_X\text{—}\left(\underset{R\text{-}(CH_2CH_2O)_m\text{-}(CH_2\underset{CH_3}{CH}O)_n\text{-}R'}{\overset{CH_3}{Si}}\text{-}O\text{-}\right)_Y\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Where X, Y, m and n are each a whole number ranging from 0 to 25, provided that X or Y is at least 1. X is between 0-10 and y, m and n are each preferably between 0-5. R and R' are straight chain or branched alkyl chain having from about 1 to about 25 carbon atoms, saturated or unsaturated, and the longest linear portion of the alkyl chain is 15 carbon atoms or less on the average. The fluorinated surfactant is described in the following formulae:

$F(CF_2)_n$-CH_2CH_2-S-CH_2CH_2-COOM

$F(CF_2)_n$-$N(CH_3)(CH_2)_3$-$(CH_2CH_2O)_x$ OSO_2M

$CF_3(CF_2CF_2)_n(CFCF)_m$-$(CH_2CH_2O)_x$-OPO_3M_2

Wherein n, m and x are integers having a value from 0 to 15; preferred values are between 1 and 12. M is a cation which makes the compound water soluble especially an alkali metal such as sodium or magnesium, ammonium or substituted ammonium cation.

Source of active oxygen

Suitable level of oxygen bleaches is in the range from 0.01 to 80% wt, preferred level is between 10 and 70% wt, ideally 30 to 60% wt. As used herein active oxygen concentration refers to the percentage concentration of elemental oxygen, with an oxidation number zero, that being reduced to water would be stoichiometrically equivalent to a given percentage concentration of a given peroxide compound, when the peroxide functionality of the peroxide compound is completely reduced to oxides. The active oxygen sources according to the present invention increase the ability of the compositions to remove oxidisable stains, to destroy malodorous molecules and to kill germs.

The concentration of available oxygen can be determined by methods known in the art, such as the iodimetric method, the permanganometric method and the cerimetric method. Said methods and the criteria for the choice of the appropriate method are described for example in "Hydrogen Peroxide", W. C. Schumo, C. N. Satterfield and R. L. Wentworth, Reinhold Publishing Corporation, New York, 1955 and "Organic Peroxides", Daniel Swern, Editor Wiley Int. Science, 1970.

Suitable organic and inorganic peroxides for use in the compositions according to the present invention include diacyl and dialkyl peroxides such as dibenzoyl peroxide, dilauroyl peroxide, dicumyl peroxide, persulphuric acid and mixtures thereof.

Suitable preformed peroxyacids for use in the compositions according to the present invention include diperoxydodecandioic acid DPDA, magnesium perphthalatic acid, perlauric acid, perbenzoic acid, diperoxyazelaic acid and mixtures thereof. Peroxygen bleaching actives useful for this invention are: percarbonates, perborates, peroxides, peroxyhydrates, persulfates. Preferred compound is sodium percarbonate and especially the coated grades that have better stability. The percarbonate can be coated with silicates, borates, waxes, sodium sulfate, sodium carbonate and surfactants cleaning at room temperature.

Bleach activators:

Optionally, the compositions may additionally comprise from 0% to 30%wt, preferably from 2% to 20%wt of peracid precursors, i.e. compounds that upon reaction with hydrogen peroxide product peroxyacids. Examples of peracid precursors suitable for use in the present invention can be found among the classes of anhydrides, amides, imides and esters such as acetyl triethyl citrate (ATC) described for instance in EP 91 87 0207, tetra acetyl ethylene diamine (TAED), succinic or maleic anhydrides.

Builders:

The detergent composition comprises contains at least one builders or a combination of them from 0.01 to 80% wt, preferably from 0.1 to 50% wt.

Examples of builders are described below:

- the parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures therefore with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.
- borate builders, as well as builders containing borate-forming materials than can produce borate under detergent storage or wash conditions can also be used.
- iminosuccinic acid metal salts
- polyaspartic acid metal salts.
- ethylene diamino tetra acetic acid and salt forms.

- water-soluble phosphonate and phosphate builders are useful for this invention. Examples of phosphate buiders are the alkali metal tripolyphosphates, sodium potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate sodium polymeta/phosphate in which the degree of polymerisation ranges from 6 to 21, and salts of phytic acid. Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from 6 to 21, and salts of phytic acid. Such polymers include the polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates.

Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivates such as the carboxymethloxysuccinates described in GB-A-1,379,241, lactoxysuccinates described in GB-A-1,389,732, and aminosuccinates described in NL-A-7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in GB-A-1,387,447.

Polycarboxylate containing four carboxy groups include oxydisuccinates disclosed in GB-A-1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarobyxlates. Polycarboxylates contining sulfo substituents include the sulfosuccinate derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and US-A-3,936448, and the sulfonated pyrolsed citrates described in GB-A-1,439,000.

Alicylic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivates of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB-A-1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Suitable polymer water-soluble compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two caroxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, and mixtures of any of thereof. The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivates such as the carboxymethloxysuccinates described in GB-A-1,379,241, lactoxysuccinates described in GB-A-1,389,732, and aminosuccinates described in NL-A-7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in GB-A-1,387,447. Polycarboxylate containing four carboxy groups include oxydisuccinates disclosed in GB-A-1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarobyxlates. Polycarboxylates contining sulfo suibstituents include the sulfosuccinate derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and US-A-3,936448, and the sulfonated pyrolsed citrates described in GB-A-1,439,000. Alicylic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivates of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB-A-1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

More preferred polymers are homo-polymers, copolymers and multiple polymers of acrylic, flourinated acrylic, sulfonated styrene, maleic anhydride, metacrylic, iso-butylene, styrene and ester monomers. Examples of these polymers are Acusol supplied from Rohm & Haas, Syntran supplied from Interpolymer and Versa and Alcosperse series supplied from Alco Chemical, a National Starch & Chemical Company.

- The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures therefore with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Examples of bicarbonate and carbonate builders are the alkaline earth and the alkali metal carbonates, including sodium and calcium carbonate and sesqui-carbonate and mixtures thereof. Other examples of carbonate type builders are the metal carboxy glycine and metal glycine carbonate.

Chelating Agent

In the context of the present application it will be appreciate that builders are compounds that sequester metal ions associated with the hardness of water, e.g.

calcium and magnesium, whereas chelating agents are compounds that sequester transition metal ions capable of catalysing the degradtaion of oxygen bleach systems. However, certain compounds may have the ability to do perform both functions.

Suitable chelating agents to be used herein include chelating agents selected from the group of phosphonate chelating agents, amino carboxylate chelating agents, polyfunctionally-substituted aromatic chelating agents, and further chelating agents like glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid, or mixtures thereof. Chelating agents when used, are typically present herein in amounts ranging from 0.01% to 50%wt of the total composition and preferably from 0.05% to 10%wt.

Suitable phosphonate chelating agents to be used herein may include ethydronic acid as well as amino phosphonate compounds, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonates. Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST TM.

Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'-disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'-disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'-disuccinic acids is, for instance, commercially available under the tradename ssEDDS TM from Palmer Research Laboratories.

Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA),N-hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanol-diglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine diacetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS TM and methyl glycine di-acetic acid (MGDA).

Fillers:

Fillers useful for the present invention are sodium chloride, bentonite, zeolites, citrates, talc and metal sulfate salts as sodium, calcium and aluminium sulfates. They can be used at a level from 0.01 to 60%wt, preferably between 0.1 to 30%wt.

Solvents:

Solvents can be used at levels of 0.01 to 50%wt, preferred level is between 0.1-5%wt. The solvent constituent may include one or more alcohol, glycol, acetate, ether acetate, glycerol, polyethylene glycol with molecular weight ranging from 200 to 10000, silicones or glycol ethers. Exemplary alcohols useful in the compositions of the invention include C2-C8 primary and secondary alcohols which may be straight chained or branched, preferably pentanol and hexanol.

Preferred solvents for the invention are glycol ethers and examples include those glycol ethers having the general structure. Preferred solvents for the invention are glycol ethers and examples include those glycol ethers having the general structure R_a-O-[CH_2-CH(R)-(CH_2)-0]$_n$-H, wherein Ra is C_{1-20} alkyl or alkenyl, or a cyclic alkane group of at least 6 carbon atoms, which may be fully or partially unsaturated or aromatic; n is an integer from 1 to 10, preferably from 1 to 5; each R is selected from H or CH_3; and a is the integer 0 or 1. Specific and preferred solvents are selected from propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol n-propyl ether, ethylene glycol n-butyl ether, diethylene glycol n-butyl ether, diethylene glycol methyl ether, propylene glycol, ethylene glycol, isopropanol, ethanol, methanol, diethylene glycol monoethyl ether acetate, and particularly useful are, propylene glycol phenyl ether, ethylene glycol hexyl ether and diethylene glycol hexyl ether.

Additional, optional, ingredients, selected from a list consisting fragrance, anticaking agent (such as sodium xylene sulfonate and magnesium sulfate), dye, enzyme are present at levels of up to 5%wt preferably less then 1%wt.

RESULTS:

The device has been compared with other foam making equipment in terms of time for foam preparation, foam consistency and convenience. The gadget efficacy in foam application onto the stain and cleaning performance have been showed against no gadget usage.

FOAM PREPARATION:

The foam has been prepared by dissolving in warm water Oxi Action Max powder, which contains foaming surfactants. About 15 grams of powder has been used with 100 ml of warm water. The solution can be prepared in a

300-500 ml open container.

The different devices are compared for preparing the foam. The reference is the spoon that can be used as mixing/aerating device.

The devices are rated in terms of timing necessary to prepare the foam, consistency of the foam, convenience in preparing the foam and cost:

Convenience Rating	**Description**	**Consistency rating**	**Foam consistency**
1	Not at all convenient	1	Much too thin/runny
2	Not very convenient	2	A little too thin/runny
3	Neither /nor	3	Just right
4	Quite convenient	4	A little too thick
5	Extremely convenient	5	Much too thick

The lower the time in making the cream the better, provided a high convenience in preparing it, high convenience rating. The consistency rating is the better, the closer to 3. Convenience in using the gadget and cream consistency have been assigned to the different gadgets through a panel test with 16 panellists.

STAIN REMOVAL TEST:

The stain removal evaluation of standard soils has been done considering Y, the reflectance value has been used for performance evaluation. The X Y Z scale has been used with a spectrophotometer with the UV-filter at 460 nm.

Y = 100 means a complete stain removal.

Standard prepared stains have been used for the test.

Standard stains (aged stain):

Soil	Type of fabric	Soil code	Supplier*
Lipstick	Cotton	Empa 141	Empa Institute
Fat/quartz	Cotton	Empa 120	Empa Institute
Salad dressing	Cotton	CFT CS-6	CFT Institute
Sebum	Cotton	WFK 10D	WFK Institute
Make up	Cotton	Empa 143	Empa Institute
Olive oil	Cotton	Empa 101	Empa Institute

*Empa Test Materials in Switzerland
WFK Testgewebe GmbH in Germany
C.F.T.-Center For Test materials B.V. in The Netherlands

The cleaning procedure is done by applying the cream to the stain, leave it for 10 minutes and then rinsing with water. In case of gadget use the cream application is done with the gadget and then three scrubbing actions are done back and forward with the cellular plastic device.

EXAMPLES:

The cellular plastic device described for preparing the foam was compared to the simple mixing with the spoon, with a hand propeller system, with a 'cappuccino cream maker', with a shaker and with a battery powered mixer. In all cases 15 grams of Oxi Action Max powder has been dissolved in 100 ml of warm water, prior to using the devices.

The cellular plastic device cleaning performance has been compared to just applying the foam onto the stain with a spoon and then rinsing.

		Table 1
Product	**Gadget name**	**Description**
Ex 1	cellular plastic device	Handle composed of two pieces, made of polyethylene, disk made of polystyrene and polyurethane/polyester cellular plastic
Ref 1	Spoon	Stainless steel spoon.
Ref 2	Propeller	A plastic handle with a propeller made of polypropylene.

Ref 3	Cappuccino cream maker	Glass container with a piston fitting with the container. At the extremity of the piston a filter is applied. This system is used up and down.
Ref 4	Shaker	Stainless steel shaker for cocktails.
Ref 5	Battery powered	Small battery powered propeller

EXAMPLE RESULTS:

Foams were prepared by dissolving 15 g in 100 ml of warm water, using Ex 1 and Ref from 1 to 5 gadgets.

Results for foam preparation:

	Foam preparation				
	Time (seconds)	**Consistency rating**	**Convenience rating**	**Cost**	**Multi-use***
Ex 1	15-30	2.9	4.1	Cheap	Yes
Ref 1	120	1.8	1.8	Cheap	NO
Ref 2	30	2.8	3.1	Cheap	NO

Ref 3	30	2.9	3.9	Expensive	NO
Ref 4	60	2.2	3.8	Medium cost	NO
Ref 5	15	3.0	4.6	Very expensive	NO

* Multi-use: can be used for foam preparation, application onto the stain and for cleaning through scrubbing.

The cellular sponge gadget is a manual system that has been rated as the more convenient among the different manual tools, it is very effective in preparing the foam, short time and good foam consistency. The cellular plastic device is in addition quite cheap and it can be used also for foam application onto the stain and for improving the cleaning performance.

Results for stain removal:

The cellular plastic device of the present invention was been used to prepare the foam by dissolving 15 g of Vanish Oxi Action Max in 100 ml of water and compared to the use of the spoon. In both cases two grams of the foam were applied onto each standard soiled swatch. In the case of the cellular plastic device 3 scrubbing back and forwards have been conducted on each swatch. Then the foam was left for 10 minutes before rinsing with cold water. After 10 minutes of the foam action all samples were rinsed.

For each device /stain for replicates were performed and the values reported in the table below are the average.

	Y - Reflectance	
Stains	**Ex 1**	**Ref 1**
Lipstick	38,1	37,6
Fats/quartz	37,9	32,8
Salad dressing	40,1	37,5
Sebum	51,6	49,8
Make up	68,9	59,4
Oilive oil	23,3	19,3

*** Ref 1 = spoon**

There is a visible cleaning improvement in using the cellular plastic device. This is due to two factors: the scrubbing action and the adsorption of the foam into the stain.

Stable Foam Formation

The stable foam is prepared by dissolving the cleaning formulation , from 1 to 50 grams in 100 ml of water, preferably between 10 and 30 grams into 100ml of water.

The stable foam is formed due to the source of active oxygen evolving oxygen within a surfactant.

RESULTS:

The foam described in this invention have been tested in terms of stain removal and colour safety, using Oxy Magic and Oxiclean as references.

STAIN REMOVAL TEST:

The stain removal evaluation of standard soils has been done considering Y, the reflectance value has been used for performance evaluation. The X Y Z scale has been used with a spectrophotometer with the UV-filter at 460 nm.

Y = 100 means a complete stain removal.

Standard prepared stains have been used for the test.

Standard stains (aged stain):

Soil	**Type of soil**	**Type of fabric**	**Soil code**	**Supplier***
Grass	Oxidisable/ proteolytic	Cotton	Empa 164	Empa Institute
Ketchup	Oxidisable	Cotton	WFK10T	WFK Institute
Lipstick	Greasy	Cotton	Empa 141	Empa Institute
Salad dressing	Greasy	Cotton	CFT CS-6	CFT Institute
Sebum	Greasy	Cotton	WFK 10D	WFK Institute
Fats/quartz	Greasy	Cotton	Empa 120	Empa Institute

*Empa Test Materials in Switzerland
WFK Testgewebe GmbH in Germany
C.F.T.-Center For Test materials B.V. in The Netherlands

The cleaning procedure is performed by applying the foam to the stain, leave it for 10 minutes and then rinsing with water.

COLOUR DAMAGE TEST:

To check for possible colour damage to dyed fabric the cleaning procedure has been done with a 30 minute contact time of the foam on coloured swatches and a high concentrated foam obtained by dissolving 30 grams of cleaning product with 100 ml of warm water. Oxiclean formulation has been used as a reference of a product well established in the market.

Type of fabric	Type of colour	Supplier*
Cotton	Red direct	WFK Institute
Cotton	Red reactive	WFK Institute
Cotton	Blue direct	WFK Institute
Cotton	Blue reactive	WFK Institute
Cotton	Yellow direct	Other supplier
Cotton	Yellow reactive	WFK Institute

*WFK Testgewebe GmbH in Germany

The colour safety has been measured by instrumental readings.

The instrumental analysis has been carried out considering delta E values between the unwashed and the washed fabric swatches.

The L*a*b* scale has been used with a spectrophotometer with the UV-filter at 460 nm. ΔE is defined as per each coloured fabric considered as:

$$\Delta E = [(L_c^* - L_w^*)^2 + (a^*_c - a^*_w)^2 + (b_c^* - b_w^*)^2]^{1/2}$$

Where:
L* = reflectance
a* = redness/greenness
b* = yellowness/blueness
c = unwashed coloured fabric
w = washed coloured fabric

ΔE equals 0 means no colour damage and in general the lower the value the lower the colour damage.

EXAMPLES:

The foams described in this invention were prepared by using powder formulations easily produced by mixing in a suitable container the ingredients. The foam was prepared by dissolving 15 grams of the cleaning formulation of this invention in 100 ml of warm water (40°C) and mixing for 3 minutes. The foam was applied for 10 minutes before rinsing with cold water (20°C). Product available on the market, Oxy Magic from Dr. Beckmann and Oxiclean new from Orange glo were used as references. These two products have been tested with the same procedure even if it was not possible to make a stable foam, but only a solution or a slightly foaming solution.

	Table 1		
Components	**Ex 1**	**Ex 2**	**Ex 3**
	%	%	%
Petro 11	0.5	0.5	0.5
Crodasinic LS95	0.5	0.5	0.5
Alkyl sulfate	3.0	3.0	3.0
Lialet 125-5	2.0	2.0	2.0
PCB S-141	40.0	55.0	20.0
TAED	3.0	-	6,5
Sodium sulfate	15.7	-	32,2
SXS 90%	0.3	0.3	0.3
Sodium carbonate	35.0	38,7	35,0

	Table 4
Component	**Description of component**
Petro 11 p	Alkyl naphthalene sulfonate from Akzo Nobel
Crodasinic LS95	Lauroyl sarcosinate from Croda
Alkyl sulfate	Sulfopon 1218-G from Cognis
Lialet 125-5	Alcohol ethoxylate from Sasol
PCB S-141	Sodium percarbonate coated from Solvay
TAED	Mykon ATC white from Warwick
SXS 90%	Sodium xylene sulfonate from Huntsman
Sodium sulfate	Sodium sulfate from different suppliers
Sodium carbonate	Sodium carbonate from different suppliers

EXAMPLE RESULTS:

Foams were prepared by using Ex 1, 2 and 3, for all dissolving 15 g and 30 grams in 100 ml of warm water and mixing for 3 minutes.

Results for stain removal:

The formulation of present invention have been used as a foam by dissolving 15 g in 100 ml of water and applying 2 ml of the foam onto each stain. After 10 minutes of contact with the foam all samples were rinsed. The reference products were used at the same dosage. Four replicates were made and the values reported in the table below is the average.

	Y - Reflectance					
	Sebum	**Lipstick**	**Salad dressing**	**Fats/quartz**	**Grass**	**Ketchup**
Ref 1	45,3	33,7	35,2	27,7	52,4	72,6
Ref 2	45,2	35,7	35,5	33,8	54,3	71,8
Ex 2	47,7	36,8	37,1	37,6	57,0	73,9

*** Ref 1 = Oxy Magic from Dr. Beckmann ; Ref 2 = New Oxiclean from Orange glo.**

Results for colour safety:

Oxiclean powder has been used as a reference. Three replicates have been considered for each product/colour type and the values reported in the table below are averages.

	Damage test					
Product	Direct blue	Reactive blue	Direct red	Reactive red	Direct Yellow	Reactive Yellow
	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE
Ref 1	0.8	1.1	1.7	0.5	0.8	1.2
Ex 2*	0.6	2.0	2.0	1.8	1.2	1.1
Ex 2**	0.7	2.0	2.5	2.2	1.3	1.1

Ref 1 = Oxiclean from Orange glo.

*** foam made with 15 grams of Ex2 in 100 ml water**

**** foam made with 30 grams of Ex2 in 100 ml water**

A value of delta E below 3.0 can be considered as no colour damage.

Claims

1. A method of cleaning stains on a soft surface the method comprising dissolving a solid cleaning formulation in water, the formulation comprising a source of active oxygen and at least one surfactant with water to form a stable foam, applying the foam directly onto the stained soft surface and cleaning the fabric in a fabric ???machine, with or without the addition of a fabric detergent, or mixing with water the stable foam formulation from the soft surface.

2. A method as claimed in claim 1 wherein the stable foam is generated by an aeration device.

3. A method as claimed in claim 1 wherein the device is a whisk.

4. A method as claimed in claim 2 wherein the aeration device is in the form of a cellular plastic.

5. A method as claimed in claim 4 wherein the aeration device is attached along at least part of one surface to a rigid support.

6. A method as claimed in claim 5 wherein the aeration device has a handle.

7. A method as claimed in claim 6 wherein the handle is attached to the opposing face of the rigid support attached to the cellular cellular sponge.

8. A method as claimed in any preceding claim wherein the soft surface is fabric.

9. A method as claimed in any preceding claim wherein an additional subsequent step is performed of applying rubbing to the stained fabric.

10. A device for the aeration of aqueous surfactant mixtures comprising a cellular plastic attached to a rigid support surface the opposing face of the rigid support surface being removably attached to a handle.

11. A kit for treating stains on soft surfaces comprising a stain cleaning composition comprising a source of active oxygen and at least one surfactant and a device for the aerating of the cleaning composition to form a stable foam for application onto the stain.

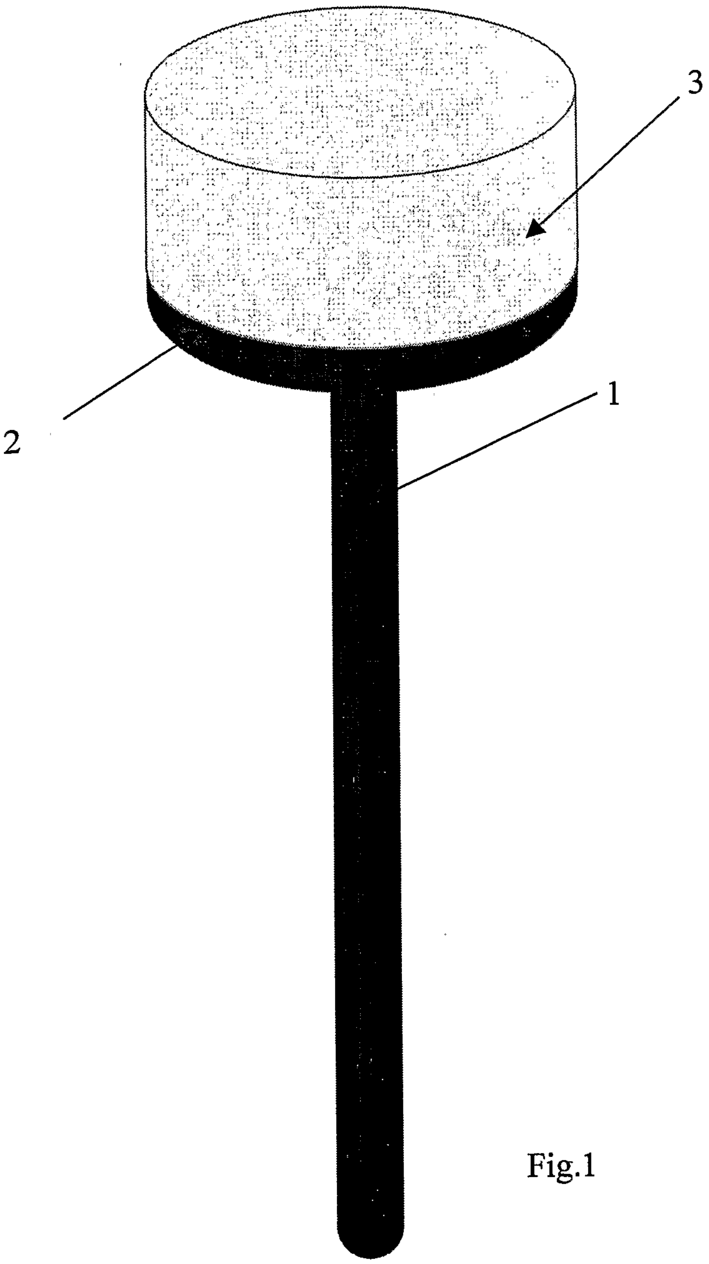


Fig.1

INTERNATIONAL SEARCH REPORT

Inte al Application No
PCT/GB2004/003979

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D11/00 C11D3/39 D06L3/02 B01F13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D D06L B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 855 217 A (JOHN ANDREAS) 5 January 1999 (1999-01-05) column 3, lines 22-36; claims	1-9
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	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 7 February 2005	Date of mailing of the international search report 28. 02. 2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Pentek, E

Form PCT/ISA/210 (second sheet) (January 2004)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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International application No.
PCT/GB2004/003979

INTERNATIONAL SEARCH REPORT

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☒ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

1-10

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-9

   Method of cleaning stains on a soft surface comprising forming a stable foam by dissolving a solid cleaning composition comprising a source of active oxygen and a surfactant, in water; applying said foam directly to the stained soft surface and cleaning the fabric.

   ---

2. claim: 10

   Device comprising a cellular plastic attached to a rigid support surface, the opposite face of the rigid support surface being removably attached to a handle.

   ---

3. claim: 11

   Kit comprising a cleaning composition comprising a source of active oxygen and a surfactant, and a device.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte nal Application No
PCT/GB2004/003979

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB2004/003979

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