METHOD OF CLEANING
SÄUBERUNGSGEFAHREN
PROCÉDE DE NETTOYAGE

Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR

Priority:
- 07.10.2003 GB 0323394
- 24.04.2004 GB 0409178

Date of publication of application:
- 21.06.2006 Bulletin 2006/25

Inventor:
DE DOMINICIS, Mattia
Montvale, NJ 07645 (US)

Representative:
Bowers, Craig Malcolm et al
Reckitt Benckiser plc
Legal Department - Patents Group
Dansom Lane
Hull
HU8 7DS (GB)

References cited:
- WO-A-00/37183
- GB-A- 2 183 461
- US-A- 6 023 810
- US-B1- 6 403 547

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).
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 comprising a source of hydrogen peroxide, such as sodium percarbonate, and at least one surfactant.

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. According to the invention there is provided 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 washing machine, with or without the addition of a fabric detergent, or mixing with water the stable foam formulation from the soft surface.

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.

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 mixing device offers particular advantages in ensuring that all of the solid composition is dissolved prior to application. This mixing is important in preventing fibre or colour damage on the soft surface since undissolved solids found on the fibre can provide for localised damage 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/m³ preferably between 20 and 80 kg/m³ 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 plastic material, and calculated in accordance with the following equation.

\[
\text{Porosity \%} = \frac{\text{apparent volume} - \text{true volume}}{\text{apparent volume}} \times 100
\]

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 (1) and cellular plastic (3), 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 are polyethylene, polypropylene, polyethylene, 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, polyethylene, 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 anti foaming agents.

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

- 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.
- 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.
- Builder, such as polyesters 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.
- Bleach activator, such as TAED, preferably at a level of 0.1 to 8%wt, preferably from 0.2 to 7%wt.
- Superwetting agent, preferably at a level from 0.01 to 10%wt.
- 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 \( R_2 SO_4 M \) 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.

[0026] 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:

[0027] Alkyl naphthalene sulfonate anionic surfactants are described in the formula below:

\[ R \text{SO}_3 M \]

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.

Alkyl naphthalene sulfonate:

[0028] Oleoyl sarcosinates are described below:

\[
\begin{align*}
\text{O} & \\
\text{R-Ch}_2\text{CH}_2& \text{C-NH (R}^1\text{) CH}_2 \text{-C-OO-M} \\
\text{O} & 
\end{align*}
\]

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, \( NR_x \) and \( x \) is from 0 to about 4.

Additional surfactants:

[0029] 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.

[0030] The nonionic surfactant is preferably a surfactant having a formula \( RO(CH_2CH_2O)_nH \) 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.

[0031] Other examples of nonionic surfactants include primary alcohol ethoxylates (available under the Neodol trade-name 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, a's 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.

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

Preferred anionic surfactants are frequently provided as alkali metal salts, ammonium salts, amine salts, amidoalcohol 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, alkylarylsulphonates, olefinsulfonates, paraffin sulfonates, alkyl sulfo succinates, alkyl ether sulfo succinates, alkylamido sulfo succinates, alkyl sulfo acetates, 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.

Preferred anionic surfactants are frequently provided as alkali metal salts, ammonium salts, amine salts, amidoalcohol 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, alkylarylsulphonates, olefinsulfonates, paraffin sulfonates, alkyl sulfo succinates, alkyl ether sulfo succinates, alkylamido sulfo succinates, alkyl sulfo acetates, 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 fluoro surfactants. The silicone glycol copolymers are described by the following formulae:

\[
\begin{align*}
\text{F(CF}_2\text{)}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{Si-O-CH}_3 \\
\text{F(CF}_2\text{)}_n\text{N(CH}_3\text{)}(\text{CH}_2\text{)}_3\text{OSO}_2\text{M}
\end{align*}
\]

\[
\text{CF}_3\text{(CF}_2\text{CF}_2)_m\text{(CFCF)}_n\text{OSO}_2\text{M}_2
\]

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.
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 diper-oxydodecandioic acid DPDA, magnesium perphthalatic acid, perlauroic acid, perbenzoic acid, diperoxyazelaic acid and mixtures thereof. Peroxygen bleaching actives useful for this invention are: percarbonates, perborates, peroxides, peroxyhydrates, persulfurates. 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.

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.

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 builders are the alkali metal tripolyphosphates, sodium potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate sodium poly-meta/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 poly-meta/phosphate in which the degree of polymerization ranges from 6 to 21, and salts of phytic acid. Such polymers include the poly-carboxylates 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 sulfanyl carboxylates.

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

[0047] Polycarboxylate containing four carboxy groups include oxydisuccinates disclosed in GB-A-1,261,829, 1,1,2,2-
5 ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates
containing sulfo substituents include the sulfosuccinate derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and

[0048] Alicyclic and heterocyclic polycarboxylates include cyclopentanone-cis,cis,cis-tetracarboxylates, cyclopentadi-
10 ene pericyclohexylates, 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

[0049] Of the above, the preferred polycarboxylates are hydroxyxcarboxylates containing up to three carboxy groups
per molecule, more particularly citrates.

[0050] 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 carboxylic 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.

[0051] Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid
and ethier 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 sulfaryl carboxylates. Polycarboxylates containing three carboxy groups
include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivates such as the
carboxymethyloxysuccinates described in GB-A-1,379,241, lactoysuccinates described in GB-A-1,389,732, and amino-
succinates described in NL-A-7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxy-
15 lates 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 tetracar-
boxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in GB-A-1,
Alicyclic and heterocyclic polycarboxylates include cyclopentanone-cis,cis,cis-tetracarboxylates, cyclopentadienide perita-
20 carboxylates, 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 derivates

[0052] Of the above, the preferred polycarboxylates are hydroxyxcarboxylates containing up to three carboxy groups
per molecule, more particularly citrates.

[0053] More preferred polymers are homo-polymers, copolymers and multiple polymers of acrylic, fluorinared acrylic,
sulfonated styrene, maleic anhydride, metacylic, 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.

[0054] 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.

[0055] Examples of bicarbonate and carbonate builders are the alkaline earth and the alkali metal carbonates, including
sodium and calcium carbonate and sesquicarbonate and mixtures thereof. Other examples of carbonate type builders
are the metal carboxy glycine and metal glycine carbonate.

Chelating Agent

[0056] 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 degradatation of oxygen bleach systems. However, certain
compounds may have the ability to perform both functions.

[0057] 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.

[0058] Suitable phosphonate chelating agents to be used herein may include ethydrionic acid as well as amino pho-
25 sonate compounds, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy dipospho-
nates, nitrilo trimethylene phosphonates, ethylene diamine tetra methane phosphonates, and diethylene triamine penta
methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different
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.

Solvants:

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 R-O-[CH2-CH(R)-(CH2)-O]n-H, wherein Ra is C1-20 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 CH3; 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.

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:

<table>
<thead>
<tr>
<th>Convenience Rating</th>
<th>Description</th>
<th>Consistency rating</th>
<th>Foam consistency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Not at all convenient</td>
<td>1</td>
<td>Much too thin/runny</td>
</tr>
<tr>
<td>2</td>
<td>Not very convenient</td>
<td>2</td>
<td>A little too thin/runny</td>
</tr>
<tr>
<td>3</td>
<td>Neither /nor</td>
<td>3</td>
<td>Just right</td>
</tr>
<tr>
<td>4</td>
<td>Quite convenient</td>
<td>4</td>
<td>A little too thick</td>
</tr>
<tr>
<td>5</td>
<td>Extremely convenient</td>
<td>5</td>
<td>Much too thick</td>
</tr>
</tbody>
</table>

[0070] 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:

[0071] 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):

[0072]

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

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

[0073] 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:

[0074] 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.

[0075] The cellular plastic device cleaning performance has been compared to just applying the foam onto the stain with a spoon and then rinsing.
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:

<table>
<thead>
<tr>
<th>Foam preparation</th>
<th>Ex 1</th>
<th>Ref 1</th>
<th>Ref 2</th>
<th>Ref 3</th>
<th>Ref 4</th>
<th>Ref 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (seconds)</td>
<td>15-30</td>
<td>120</td>
<td>30</td>
<td>30</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>Consistency rating</td>
<td>2.9</td>
<td>1.8</td>
<td>2.8</td>
<td>2.9</td>
<td>2.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Convenience rating</td>
<td>4.1</td>
<td>1.8</td>
<td>3.1</td>
<td>3.9</td>
<td>3.8</td>
<td>4.6</td>
</tr>
<tr>
<td>Cost</td>
<td>Cheap</td>
<td>Cheap</td>
<td>Cheap</td>
<td>Expensive</td>
<td>Medium cost</td>
<td>Very expensive</td>
</tr>
<tr>
<td>Multi-use*</td>
<td>Yes</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>

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

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.

<table>
<thead>
<tr>
<th>Y - Reflectance</th>
<th>Stains</th>
<th>Ex 1</th>
<th>Ref 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lipstick</td>
<td>38.1</td>
<td>37.6</td>
<td></td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Soils</th>
<th>Supplier*</th>
<th>Type of soil</th>
<th>Supplier*</th>
<th>Soil code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grass</td>
<td>Empa Test Materials in Switzerland</td>
<td>Oxidisable/ proteolytic</td>
<td>Empa Institute</td>
<td>Empa 164</td>
</tr>
<tr>
<td>Ketchup</td>
<td>WFK Testgewebe GmbH in Germany</td>
<td>Greasy</td>
<td>WFK Institute</td>
<td>WFK10T</td>
</tr>
<tr>
<td>Lipstick</td>
<td>C.F.T.-Center For Test materials B.V. in The Netherlands</td>
<td>Greasy</td>
<td>C.F.T.-Center For Test materials B.V. in The Netherlands</td>
<td>CFT CS-6</td>
</tr>
<tr>
<td>Salad dressing</td>
<td>Greasy</td>
<td>Cotton</td>
<td>Empa Institute</td>
<td>Empa 141</td>
</tr>
<tr>
<td>Sebum</td>
<td>Greasy</td>
<td>Cotton</td>
<td>WFK Institute</td>
<td>WFK 10D</td>
</tr>
<tr>
<td>Fats/quartz</td>
<td>Greasy</td>
<td>Cotton</td>
<td>Empa Institute</td>
<td>Empa 120</td>
</tr>
</tbody>
</table>

* Ref 1 = spoon

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:

[0088] 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.

<table>
<thead>
<tr>
<th>Type of fabric</th>
<th>Type of colour</th>
<th>Supplier*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>Red direct</td>
<td>WFK Institute</td>
</tr>
<tr>
<td>Cotton</td>
<td>Red reactive</td>
<td>WFK Institute</td>
</tr>
<tr>
<td>Cotton</td>
<td>Blue direct</td>
<td>WFK Institute</td>
</tr>
<tr>
<td>Cotton</td>
<td>Blue reactive</td>
<td>WFK Institute</td>
</tr>
<tr>
<td>Cotton</td>
<td>Yellow direct</td>
<td>Other supplier</td>
</tr>
<tr>
<td>Cotton</td>
<td>Yellow reactive</td>
<td>WFK Institute</td>
</tr>
</tbody>
</table>

*WFK Testgewebe GmbH in Germany

[0089] The colour safety has been measured by instrumental readings.

[0090] The instrumental analysis has been carried out considering delta E values between the unwashed and the washed fabric swatches.

[0091] The L* a*b* scale has been used with a spectrophotometer with the UV-filter at 460 nm. \( \Delta E \) is defined as per each coloured fabric considered as:

\[
\Delta E = \left[ (L_c^* - L_w^* )^2 + (a_c^* - a_w^*)^2 + (b_c^* - b_w^*)^2 \right]^{1/2}
\]

Where:

- \( L^* \) = reflectance
- \( a^* \) = redness/greenness
- \( b^* \) = yellowness/blueness
- \( c \) = unwashed coloured fabric
- \( w \) = washed coloured fabric

[0092] \( \Delta E \) equals 0 means no colour damage and in general the lower the value the lower the colour damage.

EXAMPLES:

[0093] 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>
<thead>
<tr>
<th>Components</th>
<th>Ex 1</th>
<th>Ex 2</th>
<th>Ex 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petro 11</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Crodasinic LS95</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Alkyl sulfate</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Components</th>
<th>Ex 1</th>
<th>Ex 2</th>
<th>Ex 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Lialet 125-5</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>PCB S-141</td>
<td>40.0</td>
<td>55.0</td>
<td>20.0</td>
</tr>
<tr>
<td>TAED</td>
<td>3.0</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>15.7</td>
<td>-</td>
<td>32.2</td>
</tr>
<tr>
<td>SXS 90%</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>35.0</td>
<td>38.7</td>
<td>35.0</td>
</tr>
</tbody>
</table>

Table 4

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

<table>
<thead>
<tr>
<th>Y - Reflectance</th>
<th>Sebum</th>
<th>Lipstick</th>
<th>Salad dressing</th>
<th>Fats/quartz</th>
<th>Grass</th>
<th>Ketchup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref 1</td>
<td>45.3</td>
<td>33.7</td>
<td>35.2</td>
<td>27.7</td>
<td>52.4</td>
<td>72.6</td>
</tr>
<tr>
<td>Ref 2</td>
<td>95.2</td>
<td>35.7</td>
<td>35.5</td>
<td>33.8</td>
<td>54.3</td>
<td>71.8</td>
</tr>
<tr>
<td>Ex 2</td>
<td>47.7</td>
<td>36.8</td>
<td>37.1</td>
<td>37.6</td>
<td>57.0</td>
<td>73.9</td>
</tr>
</tbody>
</table>

*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.

<table>
<thead>
<tr>
<th>Product</th>
<th>Direct blue</th>
<th>Reactive blue</th>
<th>Direct red</th>
<th>Reactive red</th>
<th>Direct Yellow</th>
<th>Reactive Yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref 1</td>
<td>0.8</td>
<td>1.1</td>
<td>1.7</td>
<td>0.5</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Ex 2*</td>
<td>0.6</td>
<td>2.0</td>
<td>2.0</td>
<td>1.8</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Ex 2**</td>
<td>0.7</td>
<td>2.0</td>
<td>2.5</td>
<td>2.2</td>
<td>1.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

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 washing 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.

Patentansprüche

2. Verfahren nach Anspruch 1, wobei der stabile Schaum durch eine Vorrichtung zur Luftbeimischung gebildet wird.
3. Verfahren nach Anspruch 1, wobei die Vorrichtung ein Quirl ist.
4. Verfahren nach Anspruch 2, wobei die Vorrichtung zur Luftbeimischung in Form eines Schaumkunststoffs vorliegt.
5. Verfahren nach Anspruch 4, wobei die Vorrichtung zur Luftbeimischung entlang zumindest eines Teils einer Oberfläche eines starren Trägers angebracht ist.
6. Verfahren nach Anspruch 5, wobei die Vorrichtung zur Luftbeimischung einen Griff aufweist.
7. Verfahren nach Anspruch 6, wobei der Griff an der gegenüberliegenden Oberfläche des an dem Schaumschwamm angebrachten starren Trägers angebracht ist.
8. Verfahren nach einem der vorangehenden Ansprüche, wobei die weiche Oberfläche ein Gewebe ist.

Revondevcations

1. Procédé pour éliminer les taches sur une surface souple, le procédé comprenant la dissolution d’une formulation nettoyante solide dans de l’eau, la formulation comprenant une source d’oxygène actif et au moins un agent tensioactif avec de l’eau pour former une mousse stable, l’application de la mousse directement sur la surface souple tachée et le nettoyage de l’étoffe dans une machine à laver le linge, avec ou sans addition d’un détergent pour étoffes, ou le mélange à de l’eau de la formulation de mousse stable de la surface souple.

2. Procédé suivant la revendication 1, dans lequel la mousse stable est engendrée par un dispositif d’aération.
3. Procédé suivant la revendication 1, dans lequel le dispositif est un fouet.
4. Procédé suivant la revendication 2, dans lequel le dispositif d’aération est sous forme d’une matière plastique cellulaire.
5. Procédé suivant la revendication 4, dans lequel le dispositif d’aération est fixé le long d’au moins une partie d’une surface à un support rigide.
6. Procédé suivant la revendication 5, dans lequel le dispositif d’aération comporte un manche.
7. Procédé suivant la revendication 6, dans lequel le manche est fixé à la face opposée du support rigide fixé à l’éponge cellulaire.
8. Procédé suivant l’une quelconque des revendications précédentes, dans lequel la surface souple est une étoffe.
9. Procédé suivant l’une quelconque des revendications précédentes, dans lequel est mise en oeuvre une étape ultérieure supplémentaire consistant à frotter l’étoffe tachée.
REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader’s convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 91870207 A [0043]
- GB 1379241 A [0046] [0051]
- GB 1389732 A [0046] [0051]
- NL 7205873 A [0046] [0051]
- GB 1387447 A [0046] [0051]
- GB 1261829 A [0047] [0051]
- GB 1398421 A [0047] [0051]

- GB 1398422 A [0047] [0051]
- US 3936448 A [0047] [0051]
- GB 1439000 A [0047] [0051]
- US 1425343 A [0048] [0051]
- US 3812044 A, Connor [0059]
- US 4704233 A, Hartman and Perkins [0060]

Non-patent literature cited in the description