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(54) **PROCESS FOR REMOVING FATTY STAINS, AND FORMULATION SUITABLE FOR SUCH PROCESS**

(57) Process for removing fatty stains, comprising the step of
(a) applying a formulation comprising
(A) at least one compound according to general formula (I)

$$R^1\text{-}O\text{-}C(O)\text{-}A^1\text{-}COO\text{-}R^1 \qquad (I)$$

wherein
R^1 are identical or different and selected from C_3-C_{10}-alkyl,
A^1 is selected from C_2-C_{18}-alkylene and C_5-C_8-cycloalkylene,

(B) at least one anionic surfactant, and
(C) at least one organic substance bearing at least one hydroxyl group and at least one amino group per molecule.

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Description

[0001] The present invention is directed towards a process for removing fatty stains, comprising the step of

(a) applying a formulation comprising

(A) at least one compound according to general formula (I)

$$R^1\text{-}O\text{-}C(O)\text{-}A^1\text{-}COO\text{-}R^1 \qquad (I)$$

wherein

R^1 are identical or different and selected from C_3-C_{10}-alkyl,
A^1 is selected from C_2-C_{18}-alkylene and C_5-C_8-cycloalkylene,

(B) at least one anionic surfactant, and
(C) at least one organic substance bearing at least one hydroxyl group and at least one amino group per molecule.

[0002] In addition, the present invention is directed towards formulations suitable for such process.

[0003] The removal of greasy stains from numerous types of surfaces is an objective of current interest. It is particularly difficult to remove such greasy stains after their thermal treatment. Examples are greasy stains in ovens that have been treated at temperatures in the range of 200°C or higher. Current cleaners available on the market are mostly solvent based, for example oven cleaners, stain removal concentrates, polishing pastes and insect removers. A lot of currently used cleaners contains amyl alcohol, a poorly water-soluble alcohol with a boiling point of 137 to 139°C at normal pressure.

[0004] However, legislation wishes to reduce the exposition of humans to volatile organic solvents (VOC). Therefore, there is a strong demand for a process that allows to remove greasy stains from surfaces of all kinds with formulations of less volatile organic compound content.

[0005] Accordingly, the process defined at the outset has been found, said process also being referred to as inventive process or as process according to the invention in the context with the current application.

[0006] The inventive process may comprise various steps. In any case, the inventive process comprises the step (a) of applying a formulation comprising

(A) at least one compound according to general formula (I)

$$R^1\text{-}O\text{-}C(O)\text{-}A^1\text{-}COO\text{-}R^1 \qquad (I)$$

wherein

R^1 are identical or different and selected from C_3-C_{10}-alkyl,
A^1 is selected from C_2-C_{18}-alkylene and C_5-C_8-cycloalkylene,

(B) at least one anionic surfactant, and
(C) at least one organic substance bearing at least one hydroxyl group and at least one amino group per molecule.

[0007] In the context of the present invention, said step is also being referred to as step (a) and the formulation applied herein as inventive formulation.

[0008] The inventive process is directed towards the removal of fatty stains. Fatty stains include stains from oil and from solid fats, preferably they are selected from fatty stains in ovens and fatty stains on textile. The ingredients of the inventive formulations and the details of the inventive process are defined in more detail below.

[0009] In step (a) of the inventive process, a formulation is applied that contains at least one compound according to general formula (I)

$$R^1\text{-}O\text{-}C(O)\text{-}A^1\text{-}COO\text{-}R^1 \qquad (I),$$

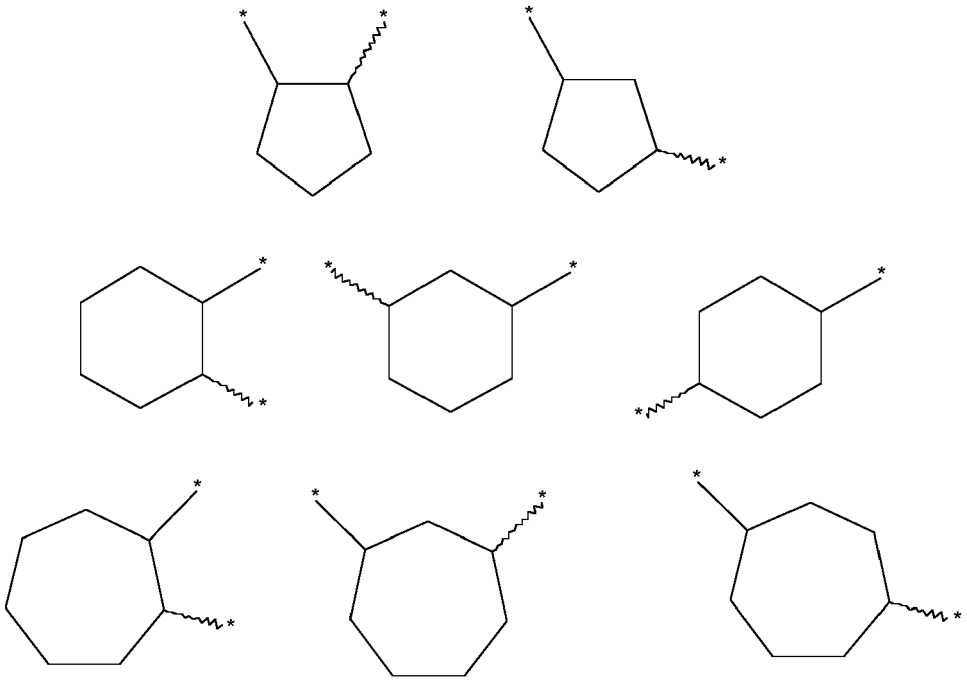
hereinafter also referred to as compound (A), wherein

[0010] R^1 are identical or different and selected from C_3-C_{10}-alkyl, for example n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl or isodecyl, preferred are in each case the n-C_3-C_{10}-alkyl groups.

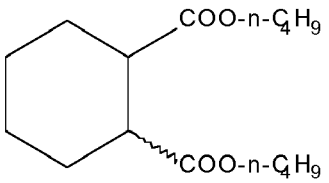
[0011] In one particular embodiment of the present invention, both R^1 in compound (A) are identical and selected from C_4-C_{10}-alkyl with at most one branching per R^1. In a preferred embodiment, both groups R^1 in compound (A) are identical and selected from n-C_3-C_{10}-alkyl. More preferred, both groups R^1 in compound (A) are identical and selected from n-C_3-C_6-alkyl. In an even more preferred embodiment, both R^1 are n-butyl.

[0012] A^1 is selected from C_2-C_{18}-alkylene and C_5-C_8-cycloalkylene. Examples of C_2-C_{18}-alkylene are $-CH_2-CH_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-CH_2-CH(CH_3)-CH_2-$, $-CH_2-C(CH_3)_2-CH_2-$, $-(CH_2)_5-$, $-(CH_2)_6-$, $-(CH_2)_7-$, $-(CH_2)_8-$, $-(CH_2)_9-$, $-(CH_2)_{10}-$, $-(CH_2)_{12}-$, $-(CH_2)_{14}-$, $-(CH_2)_{16}-$, $-(CH_2)_{18}-$.

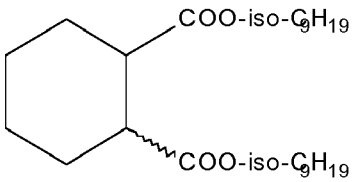
[0013] Examples of C_5-C_8-cycloalkylene are cyclopenylene, cyclohexylene, cycloheptylene and cyclooctylene, in particular of the following formulae:



[0014] Particularly preferred examples of compounds (A) are di-n-butylsuccinate, di-n-hexylsuccinate, di-n-butyladipate, di-n-hexyl adipate, and

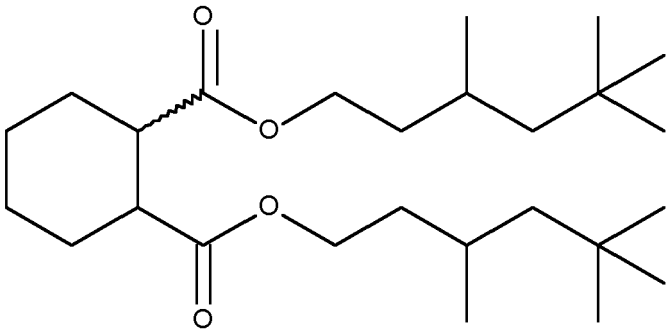


mixture of cis- and trans



mixture of cis- and trans

Even more preferred is



mixture of cis- and trans

[0015] Formulations used in step (a) of the inventive process comprise at least one anionic surfactant (B). Examples of suitable anionic surfactants (B) are alkali metal and ammonium salts of C_8-C_{12}-alkyl sulfates, of C_{12}-C_{18}-fatty alcohol ether sulfates, of C_{12}-C_{18}-fatty alcohol polyether sulfates, of sulfuric acid half-esters of ethoxylated C_4-C_{12}-alkylphenols (ethoxylation: 3 to 50 mol of ethylene oxide/mol), of C_{12}-C_{18}-alkylsulfonic acids, of C_{12}-C_{18} sulfo fatty acid alkyl esters, for example of C_{12}-C_{18} sulfo fatty acid methyl esters, of C_{10}-C_{18}-alkylarylsulfonic acids, preferably of n-C_{10}-C_{18}-alkylbenzene sulfonic acids, of C_{10}-C_{18} alkyl alkoxy carboxylates and of soaps such as for example C_8-C_{24}-carboxylic acids. Preference is given to the alkali metal salts of the aforementioned compounds, particularly preferably the sodium salts.

[0016] In one embodiment of the present invention, anionic surfactants (B) are selected from n-C_{10}-C_{18}-alkylbenzene sulfonic acids and from fatty alcohol polyether sulfates, which, within the context of the present invention, are in particular sulfuric acid half-esters of ethoxylated C_{12}-C_{18}-alkanols with a degree of ethoxylation in the range of from 1 to 50 mol of ethylene oxide/mol, preferably of n-C_{12}-C_{18}-alkanols.

[0017] Further examples of anionic surfactants are carboxylates that bear a linear C_{10}-C_{30}-alkyl group or a linear C_{10}-C_{30}-mono-alkenyl group, the C-C double bond being preferably trans. Examples are not only stearate and palmitate but also N-(n-C_{10}-C_{30}-alkyl) sarcosinates, for example sodium N-lauroylsarcosinate.

[0018] Formulations used in step (a) of the inventive process comprise (C) at least one organic substance bearing at least one hydroxyl group and at least one amino group per molecule, hereinafter also referred to as organic substance (C). Examples of organic substances (C) are 2-aminoethanol ("ethanolamine"), boiling point 172°C, N,N-diethanolamine, N,N,N-triethanolamine ("triethanolamine"), N-methylethanolamine, N-methyl-N,N-diethanolamine, and N-n-butyl-N,N-diethanolamine.

[0019] In one embodiment of the present invention, organic substance (C) is selected from polyalkylenimines that may be alkoxylated, and from poly-triethanolamine. Preferably, such poly-triethanolamine has a molecular weight M_n in the range of from 450 to 4,500 g/mol.

[0020] Polyalkylenimines (C) are described in more detail below.

[0021] Polyalkylenimine (C) comprises alkoxy side chains and a backbone of polyalkylenimine, for example polyethylenimine or polypropylenimine. The polyalkylenimine backbone can be linear, predominantly linear or branched, predominantly linear being preferred and linear being more preferred. The structure of the polyalkylenimine backbone is depending on the type of synthesis of the respective polyalkylenimine. In the context of the present invention, said polyalkylenimine can also be referred to as "backbone" or as "backbone of alkoxylated polyalkylenimine (C)".

[0022] Polyalkylenimines (C) as defined in the context with the present invention can also be regarded as polyalkylenepolyamines. They bear at least 6 N-atoms per molecule in the form of amino groups, e. g., as NH_2-groups, as secondary amino groups or as tertiary amino groups.

[0023] The term "polyethylenimine" in the context of the present invention does not only refer to polyethylenimine homopolymers but also to polyalkylenimines containing NH-CH_2-CH_2-NH structural elements structural elements together with other alkylene diamine structural elements, for example NH-CH_2-CH_2-CH_2-NH structural elements, NH-$CH(CH_3)$-CH2-NH structural elements, NH-$(CH_2)_4$-NH structural elements, NH-$(CH_2)_6$-NH structural elements or (NH-$(CH_2)_8$-NH structural elements but the NH-CH_2- CH_2-NH structural elements being in the majority with respect to the molar share. Preferred polyethylenimines contain NH-CH_2-CH_2-NH structural elements being in the majority with respect to the molar share, for example amounting to 60 mol-% or more, more preferably amounting to at least 70 mol-%, referring to all alkylenimine structural elements in said polyalkylenimine (C). In a special embodiment, polyethylenimine refers to those polyalkylene imines that bear one or zero alkylenimine structural element per molecule that is different from NH-CH_2-CH_2-NH.

[0024] The term "polypropylenimine" in the context of the present invention does not only refer to polypropylenimine homopolymers but also to polyalkylenimines containing NH-CH_2-CH_2-CH_2-NH structural elements or NH-CH_2-$CH(CH_3)$-NH structural elements together with other alkylene diamine structural elements, for example NH-

CH_2-CH_2-NH structural elements, NH-$(CH_2)_4$-NH structural elements, NH-$(CH_2)_6$-NH structural elements or (NH-$(CH_2)_8$-NH structural elements but the NH-CH_2-CH_2-CH_2-NH structural elements or NH-CH_2-$CH(CH_3)$-NH structural elements being in the majority with respect to the molar share. Preferred polypropylenimines contain NH-CH_2-CH_2-CH_2-NH structural elements being in the majority with respect to the molar share, for example amounting to 60 mol-% or more, more preferably amounting to at least 70 mol-%, referring to all alkylenimine structural elements in said polyalkylenimine (C). In a special embodiment, polypropylenimine refers to those polyalkylene imines that bear one or zero alkylenimine structural element per molecule that is different from NH-CH_2-CH_2-CH_2-NH.

[0025] Branches may be alkylenamino groups such as, but not limited to -CH_2-CH_2-NH_2 groups or $(CH_2)_3$-NH_2-groups. Longer branches may be, for examples, -$(CH_2)_3$-N$(CH_2CH_2CH_2NH_2)_2$ groups. Highly branched polyalkylenimines are, e.g., polypropylene dendrimers or related molecules with a degree of branching in the range from 0.25 to 0.95, preferably in the range from 0.30 to 0.80 and particularly preferably at least 0.5. The degree of branching can be determined for example by ^{13}C-NMR or ^{15}N-NMR spectroscopy, preferably in D_2O, and is defined as follows:

$$DB = D+T/D+T+L$$

with D (dendritic) corresponding to the fraction of tertiary amino groups, L (linear) corresponding to the fraction of secondary amino groups and T (terminal) corresponding to the fraction of primary amino groups.

[0026] Within the context of the present invention, highly branched polyalkylenimines are polyalkylenimines with DB in the range from 0.25 to 0.95, particularly preferably in the range from 0.30 to 0.90% and very particularly preferably at least 0.5.

[0027] In the context of the present invention, CH_3-groups are not being considered as branches.

[0028] Polyalkylenimine (C) may be non-substituted or substituted with (poly)oxyalkylene groups. Said alkoxy side chains can be attached to the backbone by alkoxylation. (Poly)oxyalkylene groups may be attached to the backbone by reacting the respective polyalkylenimine with at least one alkylene oxide, for example ethylene oxide, propylene oxide, butylene oxide, pentylenoxide, decenyl oxide, dodecenyl oxide, or mixtures of at least two alkylene oxides of the foregoing. Preference is given to ethylene oxide, 1,2-propylene oxide and mixtures of ethylene oxide and 1,2-propylene oxide. If mixtures of at least two alkylene oxides are applied they can be reacted random-wise or block-wise.

[0029] In one embodiment of the present invention, polyalkylenimine (C) is selected from those with alkylene oxide units and N atoms in a molar ratio in the range of from 1 : 1 to 100 : 1, preferably in the range of from 2:1 to 50:1, the N atoms resulting from alkylenimine units. The alkylenimine units are ethylenimine units in their majority, for example at least 60 mol-%, referring to the total of alkylenimine units, preferably at least 70 mol-%.

[0030] In a special embodiment of the present invention, polyalkylenimine (C) is selected from those with alkylene oxide units and N atoms in a molar ratio in the range of from 1 : 1 to 100 : 1, preferably in the range of from 2:1 to 50:1, the N atoms resulting from ethylenimine units, and no alkylenimine units other than ethylenimine or propylenimine units being present.

[0031] In one embodiment of the present invention, the average molecular weight M_w of polyalkylenimines (C) is in the range of from 2,500 to 1,500,000 g/mol, preferably up to 500,000 g/mol and more preferably up to 100,000 g/mol. The average molecular weight M_w of polyalkylenimines (C) may be determined by gel permeation chromatography (GPC), with 1.5 % by weight aqueous formic acid as eluent and cross-linked poly-hydroxyethylmethacrylate as stationary phase.

[0032] In one embodiment of the present invention polyalkylenimines (C) display a polydispersity Q = M_w/M_n of at least 3.5, preferably in the range of from 3.5 to 10, more preferably in the range of from 4 to 9 and even more preferably from 4.0 to 5.5. In other embodiments, polyalkylenimines (C) display a polydispersity Q = M_w/M_n of 1.5 to 3.5.

[0033] Formulations used in step (a) of the inventive process may comprise water.

[0034] In one embodiment of the present invention, the formulation applied in step (a) has a total concentration of (A), (B), and (C) in the range of from 3 to 15% by weight. In other embodiments, the formulation applied in step (a) is a concentrate, and the total concentration of (A), (B), and (C) is in the range of from 80 to 99% by weight.

[0035] In a preferred embodiment of the present invention, formulations used in step (a) of the inventive process do not contain significant amounts of organic solvents with a boiling point below 145°C at normal pressure. Significant amounts in this context refers to quantities of 1 % by weight or more.

[0036] In one embodiment of the present invention, formulation applied in step (a) is an aqueous formulation that has a pH value in the range of from 6 to 14, preferably up to 13.5.

[0037] In one embodiment of the present invention, formulation used in step (a) of the inventive process contains

(D) at least one N-C_2-C_{20}-alkyl amide, hereinafter also referred to as amides (D).

[0038] Examples of amides (D) are non-cyclic and cyclic N-C_2-C_{20}-alkyl amides. Non-cyclic N-C_2-C_{20}-alkyl amides (D) include N-C_2-C_{20}-monoalkyl amides and N,N-di-C_2-C_{20}-alkyl amides. Specific examples are N-ethyl formamide, N-isopropyl formamide, and N,N-diethyl formamide. Further examples are N,N-diethyloctanamide and N,N-diethyl decanamide. Cyclic N-C_2-C_{20}-alkyl amides - hereinafter also referred to as lactams (D) - are preferred. Examples of lactams (D) are selected from γ-lactams (gamma-lactams), δ-lactams and ε-lactams. Specific examples are N-ethyl pyrrolidone, N-octyl pyrrolidone, N-ethyl 6-valerolactam, N-octyl δ-valerolactam, N-ethyl ε-caprolactam, and N-octyl ε-caprolactam.

[0039] In one embodiment of the present invention, the weight ratio of compound (A) to lactam (D) is in the range of from 1:1 to 10:1.

[0040] In one embodiment of the present invention, formulations applied in step (a) comprise

(A) in the range of from 1 to 3 % by weight compound (A),
(B) in the range of from 0.01 to 5 % by weight anionic surfactant, preferably 0.1 to 2.5 % by weight,
(C) in the range of from 0.1 to 10 % by weight organic substance (C), preferably 1 to 5 % by weight,
and, optionally,
(D) in the range of from 0.1 to 3 % by weight N-C_2-C_{20}-alkyl amide, preferably 0.5 - 2 % by weight,

percentages referring to the total respective formulation.

[0041] In embodiments in which organic substance (C) is selected from polyalkylenimines (C) inventive formulations preferably comprise 0.1 to 5 % by weigh of polyalkylenimine (C), even more preferably from 0.2 to 3 % by weight.

[0042] Step (a) of the inventive process may be carried out by contacting a soiled surface with a formulation described above. Such contacting may be carried out by pouring, spraying, dripping or the like of such formulation on said surface, or by putting the surface soiled into said formulation.

[0043] Said applying may be supported mechanically, for example by rubbing, brushing, and beating on a clean surface, preferred are rubbing and brushing, or without mechanical support.

[0044] In one embodiment of the present invention, step (a) of the inventive process is performed at a temperature in the range of from 10 to 50°C, preferably 15 to 50°C and even more preferably 20 to 40°C.

[0045] In one embodiment of the present invention, the inventive process comprises at least one step (b) that is directed to removal of non-used formulation and the removal of soil. Non-used formulation and Step (b) may be carried out by rinsing the cleaned surface with a rinse formulation, for example water or an aqueous rinse solution.

[0046] In addition, the inventive process may comprise a step (c) that is directed to drying of the cleaned surface.

[0047] In other embodiments, the inventive process is applied to soiled textile surfaces, and - as step (d) - a regular laundering step or heavy duty laundering step follows.

[0048] In other embodiments, the inventive process is applied to soiled china or soiled kitchenware, and a regular automatic dishwashing step (e) follows.

[0049] The inventive process leads to excellent cleaning results. Soil and preferably greasy soil can be removed easily and to a major extent from all sorts of surfaces, for example textile or metal surfaces.

[0050] A further aspect of the present invention is directed towards formulations that may be employed in step (a), such formulations also being referred to as inventive formulations or as formulations according to the present invention. Inventive formulations may comprise

(A) at least one compound according to general formula (I)

$$R^1\text{-O-C(O)-}A^1\text{-COO-}R^1 \qquad (I)$$

wherein

R^1 are identical or different and selected from C_3-C_{10}-alkyl,
A^1 is selected from C_2-C_{18}-alkylene and C_5-C_8-cycloalkylene,

(B) at least one anionic surfactant,
(C) at least one organic substance bearing at least one hydroxyl group and at least one amino group per molecule,
and, optionally,
(D) at least one N-C_2-C_{20}-alkyl amide.

[0051] Compounds (A), anionic surfactants (B), organic substances (C), lactams (D) and polymers (E) including their preferred embodiments have been described in more detail above.

[0052] In one embodiment of the present invention both groups R^1 in compound (A) are identical and selected from C_4-C_{10}-alkyl with at most one branching per R^1. In a more preferred embodiment of the present invention compound

(A) is selected from the di-n-butylester of adipic acid and the diisononylester of 1,2-cyclohexane dicarboxylic acid.

[0053] In one embodiment of the present invention inventive formulations are aqueous formulations that have a pH value in the range of from 6 to 14, preferably up to 13.5. Especially in embodiments wherein the surface to be cleaned is a textile surface inventive formulations with a pH value of up to 13.5 are particularly useful. In embodiments wherein surfaces are car surfaces inventive solutions with a pH value in the range of from 6 to 10 are preferred.

[0054] In one embodiment of the present invention, inventive formulations comprise

(A) in the range of from 1 to 3 % by weight compound (A),
(B) in the range of from 0.01 to 5 % by weight anionic surfactant, preferably 0.1 to 2.5 % by weight,
(C) in the range of from 0.1 to 10 % by weight organic substance (C), preferably 1 to 5 % by weight,
and, optionally,
(D) in the range of from 0.1 to 3 % by weight N-C_2-C_{20}-alkyl amide, preferably 0.5 - 2 % by weight,

percentages referring to the total respective formulation.

[0055] In embodiments in which organic substance (C) is selected from polyalkylenimines (C) inventive formulations preferably comprise from 0.1 to 5 % by weigh of polyalkylenimine (C), even more preferably from 0.2 to 3 % by weight.

[0056] In one embodiment of the present invention both R^1 in compound according to general formula (I) are identical and selected from C_4-C_{10}-alkyl with at most one branching per R^1.

[0057] Inventive formulations have excellent cleaning properties, for example as hard surface cleaners or as fabric cleaners, combined with a low demand for volatile solvents.

[0058] A specific aspect of the present invention is the use of an inventive formulation for the removal of fatty stains from collars of shirts. Another specific aspect of the present invention is the use of an inventive formulation for the removal of fatty stains from ovens.

[0059] The present invention I further illustrated by the following working examples.

Working examples

[0060] General remark: Percentages refer to % by weight unless expressly indicated otherwise.

[0061] The following ingredients were used:

(A.1): di-n-butyladipate
(A.2): di-n-hexyladipate
(A.3): 1,2-cyclohexane dicarboxylic acid diisononyl ester
(B.1): n-C_{12}-C_{14}-alkyl-O-$(CH_2CH_2O)_3$-SO_3Na
(B.2): Sodium N-lauroylsarcosinate
(B.3): Sodium laurylsulfate
(C.1): monoethanolamine
(C.2): N,N-diethanolamine
(C.3): ethoxylated polyethylenimine (PEI), M_n 2.000, 12 EO/NH
(C.4): ethoxylated polyethylenimine (PEI) M_n 25.000, 15 EO/NH
(D.1:) N-n-octylpyrrolidone
(D.2): N,N-dimethyl n-octanamide
(D.3): N-methylpyrrolidone

I. Manufacture of inventive formulations tested as hard surface cleaners

I.1. Manufacture of comparative formulation C-HSC.1

[0062] A 250 ml vessel was charged with 80 g water. Then, 6 g aqueous solution of NaOH (50%), 5 g (C.1), and 8 g butylenediglycol (BDG) were added, followed by 1 g (B.1). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Comparative formulation C-HSC.1 was obtained.

I.2. Manufacture of comparative formulation C-HSC.2

[0063] A 250 ml vessel was charged with 80 g water. Then, 5 g K_2CO_3, 1.2 g colloidal magnesium aluminium silicate, 3.5 g (C.1), 2 g (C.2), and 8 g butylenediglycol (BDG) were added, followed by 0.5 g (B.2). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Comparative formulation C-HSC.2 was obtained.

I.3. Manufacture of inventive formulation HSC.3

[0064] A 250 ml vessel was charged with 80 g water. Then, 6 g aqueous solution of NaOH (50%), 1.5 g (C.1), 0.5 g (C.2), and 2.5 g (A.1) were added, followed by 0.8 g (B.1). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.3 was obtained.

I.4. Manufacture of inventive formulation HSC.4

[0065] A 250 ml vessel was charged with 80 g water. Then, 6 g aqueous solution of NaOH (50%), 1.5 g (C.1), 0.5 g (C.2), 2.5 g (A.1), and 0.5 g (D.1) were added, followed by 0.3 g (B.3). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.4 was obtained.

I.5. Manufacture of inventive formulation HSC.5

[0066] A 250 ml vessel was charged with 80 g water. Then, 6 g aqueous solution of NaOH (50%), 1.5 g (C.1), 2.5 g (A.1), 0.3 g (D.1), and 0.8 g colloidal magnesium aluminium silicate were added, followed by 0.1 g (B.2). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.5 was obtained.

I.6. Manufacture of inventive formulation HSC.6

[0067] A 250 ml vessel was charged with 80 g water. Then, 6 g aqueous solution of NaOH (50%), 1.5 g (C.1), 3 g (A.3), 0.3 g (D.1), and 0.8 g colloidal magnesium aluminium silicate were added, followed by 0.1 g (B.2). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.6 was obtained.

I.7. Manufacture of inventive formulation HSC.7

[0068] A 250 ml vessel was charged with 80 g water. Then, 6 g aqueous solution of NaOH (50%), 1.5 g (C.1), 0.5 g (C.2), 3 g (A.2), and 0.5 g (D.1) were added, followed by 0.3 g (B.1). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.7 was obtained.

1.8. Manufacture of inventive formulation HSC.8

[0069] A 250 ml vessel was charged with 80 g water. Then, 6 g aqueous solution of NaOH (50%), 1.5 g (C.1), 2.5 g (A.1), 0.3 g (D.1), and 2 g (C.4) were added, followed by 0.1 g (B.2). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.8 was obtained.

I.9. Manufacture of inventive formulation HSC.9

[0070] A 250 ml vessel was charged with 80 g water. Then, 4 g Na_2CO_3 1.5 g Monoethanolamine, 3 g (A.2), 0.5 g (D.1), and 2.5 g (C.3) were added, followed by 0.2 g (B.2). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.9 was obtained.

I.10. Manufacture of inventive formulation HSC.10

[0071] A 250 ml vessel was charged with 80 g water. Then, 5 g K_2CO_3, 1.0 g (C.1), 2.5 g (A.1), 0.3 g (D.1), and 2.5 g (C.4) were added, followed by 0.1 g (B.2). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.10 was obtained.

I.11. Manufacture of inventive formulation HSC.11

[0072] A 250 ml vessel was charged with 80 g water. Then, 5 g K_2CO_3, 1.0 g (C.1), 2.5 g (A.1), 0.3 g (D.2), and 2.5 g (C.4) were added, followed by 0.1 g (B.2). Homogenisation was achieved with moderate stirring (magnetic) at ambient temperature over a period of time of 5 minutes. Inventive formulation HSC.11 was obtained.

II. Tests as hard surface cleaners

[0073] Performance was evaluated with respect to the cleaning performance at ambient temperature on ceramic and stainless steel surfaces.

[0074] Test soil: a greasy soil was prepared by mixing 25.0% butter, 25.0% lard, 25.0% margarine, 12.5% ketchup, and 12.5% mustard at 40 to 45°C under continuous stirring. Warm greasy soil was obtained.

[0075] White ceramic tiles (20x20 cm) with matt surface were pre-cleaned with ethanol and then their weight was determined. About 3 to 3.5 of greasy soil were applied evenly to each ceramic tile with a roller. Then, the ceramic tiles were heated in an oven to 180°C for two hours. Then, the ceramic tiles were allowed to cool to ambient temperature and stored for 48 hours. Then, the cleaning tests were performed.

[0076] inventive formulation or comparative formulation, respectively, was applied to the ceramic tile through a trigger sprayer. in each experiment an amouont of 3.5 g inventive formulation or comparative formulation, respectively, was evenly sprayed onto the surface of the respective ceramic tile. inventive formulation or comparative formulation, respectively, was allowed to act for 2 minutes. in addition, the soiled surface of the ceramic tile was wiped with a cellulose-type wet sponges (without applying any force). Then, the ceramic tile was rinsed with cold tap water. The results are summarized in Table 1.

[0077] The evaluation of the dirt removal was performed visually and refers to an average value of three experiments:

1 No removal
2 Weak removal (10-30% surface cleaned)
3 Average removal (40-70% surface cleaned)
4 Good removal (70-90% surface cleaned)
5 Excellent removal (> 90% surface cleaned)

Percentages refer to the surface.

[0078] In addition, the foaming behaviour was evaluated. A medium and stable foam formation being preferred.).

Table 1: Results of cleaning experiments

	Cleaning performance ceramic surface	Cleaning performance stainless steel surface	Product Volatiles	Foaming
C-HSC.1	3	2	1	-
C-HSC.2	2	2.5	2	0
HSC.3	4	3.5	3	0
HSC.4	4	4.5	3	+
HSC.5	4.5	4.5	3.5	+
HSC.6	4	3.5	4.5	0
HSC.7	3.5	4.5	4	0
HSC.8	5	4.5	4	+
HSC.9	4	4	4.5	+
HSC.10	4.5	4	3.5	+
HSC.11	4.5	4	3.0	+

Explanations: foaming: + means homogenous low volume and stable foam, - means inhomogeneous and/or high volume low volume stable foam formation. Rating 0: homogeneous but instable foam formation, volume acceptable.

[0079] The product volatiles were evaluated as follows: an amount of 5 g of the respective inventive formulation or comparative formulation was sprayed onto a surface that was dried at 30°C in a 40-l-vessel. Three test persons evaluated the volatiles after opening the vessel by determining the smell. Grade 5 means no smell, grade 1 means strong smell.

III. Manufacture of stain removers for textiles

III.1 Manufacture of inventive formulations

[0080] The following formulations were made by mixing the components according to Table 2 followed by adding the balance of water to 100 g.

Table 2: composition of inventive stain removers for textiles

	TSR.1	TSR.2	TSR.3
(A) [g]	(A.1) 4	(A.1) 4	(A.1) 3, (A.3) 2
(B) [g]	(B.1) 1.5	(B.2) 1.5	(B.2) 1.5
(C) [g]	(C.2) 2.5, (C.4) 2.5	(C.2) 2.5, (C.4) 2.5	(C.2) 2.5, (C.4) 2.5
(D) [g]	(D.1) 1	(D.2) 1	(D.1) 1
others	10 g isopropanol, 1 g sodium oleate	10 g isopropanol, 1 g sodium oleate	10 g isopropanol, 1 g sodium oleate

III.2 Manufacture of comparative formulation C-TSR.4

[0081] The following ingredients were mixed: 5 g of dipropyleneglycol monomethyl ether, 10 g of diethyleneglycol mono-n-butyl ether, 10 g of isopropanol, 2 g of (D.3), 1 g (B.1), 1 g sodium oleate, 3 g of n-$C_{18}H_{37}$-O(CH_2CH_2O)$_7$-H. The balance of water to 100 g was added. Comparative formulation C-TSR.4 was obtained.

IV. Textile cleaning tests

[0082] The test were performed as follows: a multi stain monitor containing 16 pieces of standardized soiled fabric, each of 2,5 x 2,5 cm size and stitched on two sides to a polyester carrier, were pre-treated with 1.5 g textile soil remover/100 cm^2 that were applied evenly. After 15 minutes of action of the textile soil remover at ambient temperature the test fabrics were laundered in a washing machine. Two test multi stain monitors were washed together with a load of 3.5 kg of cotton towels and 75 g of liquid test laundry detergent, one cycle, 40°C. The following mixture was applied as test liquid test laundry detergent:

7.7 g of n-C_{12}-C_{14}-alkyl-O-(CH_2CH_2O)$_2$-SO_3Na
5.5 g sodium salt of linear dodecylbenzenesulphonate
2.4 g coconut soap as potassium salt
2.2 g of KOH
5.4 g of n-$C_{18}H_{37}$-O(CH_2CH_2O)$_7$-H
6 g of 1,2-propylene glycol, 2 g of ethanol. The balance to 90 g was water.

[0083] The following test fabrics were used:

wfk20D: pigment and sebum-type fat on polyester/cotton mixed fabric
EMPA 101: soot and olive oil on cotton
EMPA 141/2: lipstick (8.5 g/m2) on cotton
EMPA 112: cocoa on cotton
EMPA 116: blood and milk and ink on cotton
CFT C-S-01: aged blood on cotton
CFT C-10: pigment, oil, milk on cotton
CFT C-S-10: butter on cotton

[0084] Test fabrics soiled with non-fatty stains:

EMPA 114: red wine on cotton
CFT PC-S-03: aged red wine on cotton
CFT CS-08: grass on cotton

Table 3: effect of pre-treatment with textile soil removers

	Average L-value without pretreatment	Average L-value with pretreatment	improvement > 1L
C-TSR.4	123	139	EMPA 141/2, CFT C-S-01, CFT-CS-10
TSR.1	122	152	wfk20D, EMPA 101, EMPA 141/2, CFT PC-S-03, EMPA 112, EMPA 116, CFT C-S-10
TSR.2	126	156	wfk20D, EMPA 101, EMPA 141/2, CFT PC-S-03, EMPA 112, CFT C-S-01, EMPA 116, CFT C-S-10
TSR.3	125	158	wfk20D, EMPA 101, EMPA 141/2, CFT PC-S-03, EMPA 112, CFT C-S-01, EMPA 116, CFT C-S-10

[0085] The L-value is a measure of the quality of cleaning in general and - in the instant case - of laundering compared to the non-pretreated test fabric. A difference of 1 unit can be detected by a skilled person. A non-expert can detect 2 units easily.

Claims

1. Process for removing fatty stains, comprising the step of

(a) applying a formulation comprising

(A) at least one compound according to general formula (I)

$$R^1\text{-}O\text{-}C(O)\text{-}A^1\text{-}COO\text{-}R^1 \qquad (I)$$

wherein

R^1 are identical or different and selected from C_3-C_{10}-alkyl,
A^1 is selected from C_2-C_{18}-alkylene and C_5-C_8-cycloalkylene,

(B) at least one anionic surfactant, and
(C) at least one organic substance bearing at least one hydroxyl group and at least one amino group per molecule.

2. Process according to claim 1 wherein said formulation applied in step (a) has a total concentration of (A), (B), and (C) in the range of from 3 to 15% by weight.

3. Process according to claim 1 or 2 wherein said formulation applied in step (a) additionally comprises

(D) at least one compound selected from N-C_2-C_{20}-alkyl amides.

4. Process according to any of the preceding claims wherein both R^1 in compound according to general formula (I) are identical and selected from C_4-C_{10}-alkyl with at most one branching per R^1.

5. Process according to any of the preceding claims wherein organic substance (C) is selected from polyalkylenimines, non-substituted or substituted with (poly)oxyalkylene groups.

6. Process according to claim 5 wherein polyalkylenimine (C) is selected from polyethylenimines and polypropylenimines, alkoxylated with ethylene oxide and/or propylene oxide.

7. Process according to any of the preceding claims wherein fatty stains are selected from stains in ovens and stains on textile.

8. Process according to any of the preceding claims wherein said compound according to formula (I) is selected from the di-n-butylester of adipic acid and the diisononylester of 1,2-cyclohexane dicarboxylic acid.

9. Formulation comprising

(A) at least one compound according to general formula (I)

$$R^1\text{-O-C(O)-}A^1\text{-COO-}R^1 \qquad (I)$$

wherein

R^1 are identical or different and selected from C_3-C_{10}-alkyl,
A^1 is selected from C_2-C_{18}-alkylene and C_5-C_8-cycloalkylene,

(B) at least one anionic surfactant,
(C) at least one organic substance bearing at least one hydroxyl group and at least one amino group per molecule, and, optionally,
(D) at least one N-C_2-C_{20}-alkyl amide.

10. Formulation according to claim 9 wherein said formulation is an aqueous formulation that has a pH value in the range of from 6 to 14.

11. Formulation according to claim 9 or 10 comprising

(A) in the range of from 1 to 3 % by weight compound according to general formula (I),
(B) in the range of from 0.01 to 5 % by weight anionic surfactant,
(C) in the range of from 0.1 to 10 % by weight organic substance (C), and, optionally,
(D) in the range of from 0.1 to 3 % by weight N-C_2-C_{20}-alkyl amide,

percentages referring to the total respective formulation.

12. Formulation according to any of claims 9 to 11 wherein both R^1 in compound according to general formula (I) are identical and selected from C_4-C_{10}-alkyl with at most one branching per R^1.

13. Formulation according to any of claims 9 to 12 wherein said compound according to formula (I) is selected from the di-n-butylester of adipic acid and the diisononylester of 1,2-cyclohexane dicarboxylic acid.

14. Use of a formulation according to any of claims 9 to 13 for the removal of fatty stains from collars of shirts.

15. Use of a formulation according to any of claims 9 to 13 for the removal of fatty stains from ovens.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 19 9326

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Munich	1 June 2016	Pfannenstein, Heide

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