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(54) **LAUNDERING METHOD AND LAUNDRY DETERGENT FORMULATIONS FOR IMPROVED CLEANING**

(57) The present invention relates to a method of laundering articles with improved detergency of a surfactant system comprising hydrophobic and hydrophilic sur-

factants, and to detergent systems suitable for this purpose.

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Description

Field of the invention

[0001] The present invention relates to a method of laundering articles which is directed to improve the detergency of a surfactant system used in said method, more precisely of a surfactant system comprising hydrophobic and hydrophilic surfactants, and to detergent systems suitable for this purpose.

Background of the invention

[0002] Modern laundry detergents are expected to remove a broad variety of soils and stains from laundering articles which are made from natural and artificial textile fibres alike. Over the last couple of decades, laundry detergent compositions were developed to perform improved cleaning at eco-friendly, sustainable and user-friendly conditions, such as washing performance at lower temperatures while reducing water consumption and time required for each cleaning cycle.

[0003] Modern laundry detergents generally contain a combination of different surfactants, often of different types (e.g. ionic and non-ionic) to meet the various needs and conditions (e.g. soils/stains of different natures, laundry of different materials, various washing conditions, such as washing temperatures generally ranging from 25 to 95°C or various agitation intensities (spinning speeds in washing machines), etc.), which could not be attained by a single surfactant. Nevertheless, there is still room for improvement, especially if the amount of detergent per washing operation is not to be enhanced or is even to be reduced.

[0004] The washing performance is also dependent on the method/process steps of the wash program, dose of the detergent composition, time interval of the washing cycle and types of surfactants (hydrophobic/hydrophilic) present in the detergent composition.

[0005] The processes/methods used currently for the laundering of articles do not provide optimum detergency and do not sufficiently suppress redeposition of soil on the laundering articles, leading thus to a sub-optimal performance.

[0006] Accordingly, it was an objective of the present invention to develop a new improved method for soil cleaning to maximize the detergency benefit of the surfactants. A further objective of the present invention was to provide a detergent composition with improved detergency. The method and composition should (also) be applicable to known detergents and should show improved detergency without having to increase the (overall) amount of surfactants.

Summary of the invention

[0007] The foregoing and other objectives are solved by the subject-matter of the present invention.

[0008] The present inventors found that the soil cleaning process is dependent on the Hydrophilic-Lipophilic Difference (HLD) profile of laundry (to be more precise of the surfactant composition in the wash liquor). The shifting of HLD to more negative values, e.g. from slightly positive or, ideally, slightly negative to more negative throughout the laundry process (e.g. starting from roughly $-3.5 \leq \text{HLD} \leq +1.5$, or from roughly $-1 \leq \text{HLD} \leq +0.2$ at the beginning of the wash cycle and proceeding to roughly $-5 \leq \text{HLD} \leq -0.5$ or to roughly $-4 \leq \text{HLD} \leq -2$ after step d) (or step c) if step d) has not been carried out-see below information on these steps), where the final HLD value is lower by at least 0.2 than the initial HLD value, leads to improved detergency and reduced redeposition.

[0009] Surprisingly it was found that a method of laundering articles of the present invention involving dosing of a surfactant system comprising hydrophobic and hydrophilic surfactants at defined time intervals of the wash cycle in such a way that the HLD is shifted towards more negative values over the course of the washing process provides improved detergency of the surfactant system. Alternatively expressed, in the method of the invention the surfactant system is supplied in such a way that the (overall) hydrophilicity of the surfactant system is increased in the course of the washing process (essentially by increasing the concentration of the (more) hydrophilic surfactant(s)).

[0010] Thus, according to one aspect, the present invention is directed to a method of laundering articles comprising the step of

a) providing a wash liquor, said wash liquor comprising a first surfactant system S1 that comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant,

b) applying said wash liquor to the articles to be laundered and initiating a wash cycle at a point in time T1,

c) at point in time T2 (which is after T1) supplying the wash liquor of step b), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally at least one hydrophobic surfactant, and resuming the wash cycle, and

d) if desired repeating step c) one or more times.

[0011] In another aspect, the present invention is directed to a composition comprising

i) a surfactant system S comprising a mixture of at least one hydrophobic surfactant and at least one hydrophilic surfactant, and

ii) optionally additives,

where at least 10% by weight of the hydrophilic surfactant, based on the total weight of hydrophobic and hydrophilic surfactants, is present in a delayed release form.

[0012] In another aspect, the present invention is directed to the use of said composition comprising

i) a surfactant system S comprising a mixture of at least one hydrophobic surfactant and at least one hydrophilic surfactant, and

ii) optionally additives,

where at least 10% by weight of the hydrophilic surfactant, based on the total weight of hydrophobic and hydrophilic surfactants, is present in a delayed release form,

for laundering articles.

[0013] In yet another aspect, the present invention is directed to a kit comprising at least two parts, where the first part comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant; and the second part comprises at least one hydrophilic surfactant, but no hydrophobic surfactant, where the kit is capable of being used for laundering articles.

[0014] The composition as well as the kit of parts according to the invention are suitable to be used in the method according to the invention.

Detailed Description of the Invention

[0015] Before the present compositions and formulations of the invention are described, it is to be understood that this invention is not limited to particular compositions and formulations described, since such compositions and formulations may, of course, vary. It is also to be understood that the terminology used herein is not intended to be limiting, since the scope of the present invention will be limited only by the appended claims.

Definitions

[0016] Within the context of the present invention, the term "alkyl", as used herein, refers to acyclic saturated aliphatic residues, which can be linear or branched. Furthermore, unless specifically indicated, the alkyl residue is unsubstituted and includes the indicated number of carbon atoms (e.g. in the case of C₁-C₂₂-alkyl 1 to 22 carbon atoms).

[0017] Examples of linear or branched C₁-C₂₂-alkyl include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, n-hexyl, isohexyl, n-heptyl, isoheptyl, n-octyl, isooctyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl, isodecyl, 2-propylheptyl, n-undecyl, isoundecyl, n-dodecyl, isododecyl, n-tridecyl, isotridecyl, n-tetradecyl, isotetradecyl, n-pentadecyl, isopentadecyl, n-hexadecyl, isohexadecyl, n-heptadecyl, isoheptadecyl, n-octadecyl, isooctadecyl, n-nonadecyl, isononadecyl, n-eicosyl, isoeicosyl, n-heneicosyl, isoheneicosyl, n-docosyl, isodocosyl, and other structural isomers thereof. Unless specified otherwise, isoalkyl denotes a branched alkyl group of the formula -(CH₂)_{n-3}-CH(CH₃)₂, where n is the number of carbon atoms in the respective isoalkyl group. Isopropyl (n = 3) is thus -CH(CH₃)₂, isobutyl (n = 4) is -CH₂-CH(CH₃)₂, isopentyl (n = 5) is -(CH₂)₂-CH(CH₃)₂ etc. In some instances, isoalkyl, especially higher isoalkyl, e.g. of 8 or more carbon atoms, denotes however also mixtures of various branched alkyl groups as they result from technical processes, generally containing the proper isoalkyl group as defined above in admixture with one or more other branched isomer (as is often the case, for example, for isoalkanols; see below).

[0018] Examples of linear or branched C₆-C₃₀-alkyl include, but are not limited to, n-hexyl, isohexyl, n-heptyl, isoheptyl, n-octyl, isooctyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl, isodecyl, 2-propylheptyl, n-undecyl, isoundecyl, n-dodecyl, isododecyl, n-tridecyl, isotridecyl, n-tetradecyl, isotetradecyl, n-pentadecyl, isopentadecyl, n-hexadecyl, isohexadecyl, n-heptadecyl, isoheptadecyl, n-octadecyl, isooctadecyl, n-nonadecyl, isononadecyl, n-eicosyl, isoeicosyl, n-heneicosyl, isoheneicosyl, n-docosyl, isodocosyl, n-tricosyl, isotricosyl, n-tetracosyl, isotetracosyl, n-pentacosyl, isopentacosyl, n-

hexacosyl, isohexacosyl, n-heptacosyl, isoheptacosyl, n-octacosyl, isooctacosyl, n-nonacosyl, isononacosyl, n-triacontyl, isotriacontyl, and other structural isomers thereof.

[0019] Examples of linear or branched C_4 - C_{22} alkyl include, but are not limited to, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, n-hexyl, isohexyl, n-heptyl, isoheptyl, n-octyl, isooctyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl, isodecyl, 2-propylheptyl, n-undecyl, isoundecyl, n-dodecyl, isododecyl, n-tridecyl, isotridecyl, n-tetradecyl, isotetradecyl, n-pentadecyl, isopentadecyl, n-hexadecyl, isohexadecyl, n-heptadecyl, isoheptadecyl, n-octadecyl, isooctadecyl, n-nonadecyl, isononadecyl, n-eicosyl, isoeicosyl, n-heneicosyl, isoheneicosyl, n-docosyl, isodocosyl, and other structural isomers thereof.

[0020] Examples of linear and branched C_6 - C_{22} alkyl include, but are not limited to, n-hexyl, isohexyl, n-heptyl, isoheptyl, n-octyl, isooctyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl, isodecyl, 2-propylheptyl, n-undecyl, isoundecyl, n-dodecyl, isododecyl, n-tridecyl, isotridecyl, n-tetradecyl, isotetradecyl, n-pentadecyl, isopentadecyl, n-hexadecyl, isohexadecyl, n-heptadecyl, isoheptadecyl, n-octadecyl, isooctadecyl, n-nonadecyl, isononadecyl, n-eicosyl, isoeicosyl, n-heneicosyl, isoheneicosyl, n-docosyl, isodocosyl, and other structural isomers thereof.

[0021] A linear or branched unsaturated aliphatic C_4 - C_{22} -hydrocarbon (or hydrocarbonyl) radical is a C_4 - C_{22} -alkenyl, C_4 - C_{22} -alkadienyl, C_4 - C_{22} -alkapolyenyl or C_4 - C_{22} -alkynyl radical.

[0022] C_4 - C_{22} -Alkenyl indicates monounsaturated (i.e. containing one C-C double bond) straight-chain or branched aliphatic non-cyclic hydrocarbon radicals having in general 4 to 22 carbon atoms, where the C-C double bond can be in any position. Examples are 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl, 1-ethyl-2-methyl-2-propenyl, 1-heptenyl, 2-heptenyl, 3-heptenyl, 1-octenyl, 2-octenyl, 3-octenyl, 4-octenyl, 1-nonenyl, 2-nonenyl, 3-nonenyl, 4-nonenyl, 1-decenyl, 2-decenyl, 3-decenyl, 4-decenyl, 5-decenyl etc. and the positional isomers thereof.

[0023] C_4 - C_{22} -Alkadienyl indicates straight-chain or branched aliphatic non-cyclic hydrocarbon radicals having in general 4 to 22 carbon atoms and two conjugated or isolated, but non-cumulated C-C double bonds. C_4 - C_{22} -Alkapolyenyl indicates straight-chain or branched aliphatic hydrocarbon radicals having in general 6 to 22 carbon atoms and three or more conjugated or isolated, but non-cumulated C-C double bonds. Examples for alkadi- and -polyenyl are buta-1,3-dien-1-yl, buta-1,3-dien-2-yl, penta-1,3-dien-1-yl, penta-1,3-dien-2-yl, penta-1,3-dien-3-yl, penta-1,3-dien-4-yl, penta-1,3-dien-5-yl, penta-1,4-dien-1-yl, penta-1,4-dien-2-yl, penta-1,4-dien-3-yl, and the like.

[0024] C_4 - C_{22} -Alkynyl indicates straight-chain or branched aliphatic non-cyclic hydrocarbon radicals having 4 to 22 carbon atoms and one triple bond in any position. Examples are 1-butyne, 2-butyne, 3-butyne, 1-methyl-2-propyne, 1-pentyne, 2-pentyne, 3-pentyne, 4-pentyne, 1-methyl-2-butyne, 1-methyl-3-butyne, 2-methyl-3-butyne, 3-methyl-1-butyne, 1,1-dimethyl-2-propyne, 1-ethyl-2-propyne, 1-hexyne, 2-hexyne, 3-hexyne, 4-hexyne, 5-hexyne, 1-methyl-2-pentyne, 1-methyl-3-pentyne, 1-methyl-4-pentyne, 2-methyl-3-pentyne, 2-methyl-4-pentyne, 3-methyl-1-pentyne, 3-methyl-4-pentyne, 4-methyl-1-pentyne, 4-methyl-2-pentyne, 1,1-dimethyl-2-butyne, 1,1-dimethyl-3-butyne, 1,2-dimethyl-3-butyne, 2,2-dimethyl-3-butyne, 3,3-dimethyl-1-butyne, 1-ethyl-2-butyne, 1-ethyl-3-butyne, 2-ethyl-3-butyne, 1-ethyl-1-methyl-2-propyne and the like.

[0025] C_4 - C_{18} -Alkanols are compounds R-OH, where R is C_4 - C_{18} -alkyl. Examples are n-butanol, butan-2-ol (sec-butanol), isobutanol, tert-butanol, n-pentanol, n-hexanol, n-heptanol, n-octanol, n-nonanol, n-decanol, n-undecanol, n-dodecanol, n-tridecanol, n-tetradecanol, n-pentadecanol, n-hexadecanol, n-heptadecanol, n-octadecanol, and structural isomers thereof, such as 2-ethylhexanol, 2-propylheptanol, (other) isoalkanols and (other) oxo alkanols of the corresponding carbon number.

[0026] Oxo alcohols are alcohols prepared by adding carbon monoxide (CO) and hydrogen (usually combined as synthesis gas) to an olefin to obtain an aldehyde via hydroformylation reaction and subsequent hydrogenation of the aldehyde. This results often in alcohol mixtures which can be used as such. Typical alcohols resulting from the oxo process are 2-ethylhexan-1-ol, 2-propylheptan-1-ol, 7-methyloctan-1-ol (isononyl alcohol) or 3,5,5-trimethyl-1-hexanol, but can also be mixtures, e.g. of linear and methyl-branched alcohols, or (technical) isodecyl alcohol, which is a mixture comprising 7-methyloctan-1-ol (isononyl alcohol) and 3,5,5-trimethyl-1-hexanol.

[0027] If hereinafter a group is defined to comprise at least a certain number of embodiments, this is meant to also

encompass a group which preferably consists of these embodiments only. Furthermore, unless clear from the context, the terms "first", "second", "third" or "(a)", "(b)", "(c)", "(d)" etc., and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein. In case the terms "first", "second", "third" or "(A)", "(B)" and "(C)" or "(a)", "(b)", "(c)", "(d)", "i", "ii" etc. relate to steps of a method or use or assay there is no time or time interval coherence between the steps, that is, the steps may be carried out simultaneously or there may be time intervals of seconds, minutes, hours, days, weeks, months or even years between such steps, unless otherwise indicated in the application as set forth herein above or below. T2 is however of course after T1; T3 is after T2, T4 is after T3, T5 is after T4, etc.

[0028] In the following passages, different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

[0029] Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" or "in another embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, the features, structures or characteristics may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments. Furthermore, while some embodiments described herein include some, but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art. For example, in the appended claims, any of the claimed embodiments can be used in any combination.

[0030] Soil in terms of the present invention is used in the sense of dirt, including grease, or more generally speaking to any undesired material on surfaces, including textiles, of which these are to be rid by washing/cleaning.

[0031] The terms laundering, washing and cleaning are used interchangeably in context of the present invention.

[0032] The term detergency is the ability of a detergent to remove soil from a surface by solubilizing, suspending or emulsifying it.

[0033] The term laundry includes the surfactant system, the wash liquor, and the soil, especially oil/grease, on the laundering articles (i.e. articles to be laundered or which are laundered). Also the articles to be laundered or which are laundered can be referred to as laundry. The laundering articles are articles typically subjected to a washing process with laundry detergents, such as textiles of all types, e.g. clothing, bed linen, towels, curtains, rags, textile bags, textile shoes, etc., and materials from which these are produced, such as fabric, wool or cotton balls or bales, etc.

[0034] The term wash liquor denotes a liquid, generally aqueous, medium in which textiles, or more generally articles to be laundered, are (to be) washed. A wash liquor thus comprises one or more surfactants and the liquid (generally water) in which the one or more surfactants are dissolved/suspended/dispersed. Moreover, further additives, such as those mentioned below and usually contained in commercial laundry detergents, may be present.

[0035] The term wash cycle refers to the actual washing process and comprises contacting the articles to be laundered with the wash liquor and also agitation of said articles in the wash liquor. In a washing machine, agitation of the laundry is realized by the spinning of the washing drum. In a handwashing process, agitation is realized in known ways, such as moving the laundry in the wash liquor, or bringing in friction, e.g. by rubbing the articles or washing them on a washing board.

[0036] The initiation of the wash cycle, which corresponds to the point in time T1, is that point in time when agitation starts (in case of a washing machine start of the rotation of the washing drum).

[0037] The term Hydrophilic-Lipophilic Difference (HLD) is an empirical equation that can be used to mathematically represent the microstructure of the self-assembly for a system containing surfactant, oil (in the context of laundering: fatty soil, e.g. oil/grease on the laundering articles), and aqueous phases. The HLD is a dimensionless number, where negative values indicate the presence of oil-swollen micelles distributed in a continuous aqueous phase (o/w μ E, Winsor Type I) and positive values indicate the presence of water-swollen reverse micelles dispersed in a continuous oil phase (w/o μ E, Winsor Type II). A value of zero indicates the system is at the phase inversion point, where a bicontinuous network of oil and water channels forms (Winsor Type III). Put simply, the HLD equation can robustly predict the behavior of a complex system by considering several variables, including salinity of the aqueous phase (in g/100mL), oiliness of the oil, temperature (in °C), and surfactant hydrophilicity/hydrophobicity:

$$\text{HLD} = f(S) - k(\text{EACN}) - c_T(T - 25) + \sigma \quad (1)$$

where HLD is the hydrophilic lipophilic difference, $f(S)$ is a function of salinity, S is salinity, which is expressed as g NaCl per 100 ml of aqueous solution, EACN is the effective alkane carbon number of the oil (the oil corresponding to the soil to be removed), T is the temperature in °C, and σ is the surfactant parameter (also sometimes referred to as C_c , or characteristic curvature). k and c_T are both scaling constants.

$f(S)$ and c_T are dependent on the type of surfactant (e.g., ionic, alkoxylate, Spans or APG). Spans are sorbitan ester detergents, and APGs are alkyl polyglycoside detergents. Typical values are given in table below:

Surfactant Type	$f(S)$	c_T
Ionic	$\ln(S + \text{SurfSal})$	0.01
Non-ionic surfactants except for Spans and APGs, in particular alkoxylates (e.g. ethoxylates, propoxylates, mixed ethoxylate/propoxylates, higher alkoxylates)	$0.13 \times S$	-0.06
APG or Span	~ 0	~ 0

[0038] These values can be found throughout the literature to remain relatively consistent.

[0039] The HLD principle was initially developed for enhanced oil recovery, where the salt content is distinctly higher than in laundry wash liquors. At low salt concentrations, such as is the case in laundry wash liquors, the $f(S)$ term becomes undependable, so that in the present invention the term $f(S)$ is ignored (i.e. considered as 0).

[0040] However, the values of k and σ can vary dramatically depending on the surfactant being tested because σ depends on the hydrophilicity of the surfactant head group, while the k value correlates with the hydrophobicity of the surfactant tail. k is typically between 0.06 to 0.20, and σ typically falls between -3 and 3, though some surfactants can have values for these parameters that fall outside of these ranges. k and σ can be determined experimentally; for example according to the method described on <https://www.stevenabbott.co.uk/practical-surfactants/measure-cc.php>; values can also be found in the literature, e.g. at <https://www.stevenabbott.co.uk/practical-surfactants/cc.php>. k is typically in the range of 0.15 to 0.17, except for "extended" surfactants, i.e. alkoxylated alcohols in which a fatty alcohol is first alkoxylated with a PO block (or a block of a higher alkoxide, such as butylene oxide) and then with an EO block. For the present purposes, k can be taken as 0.16, except for said extended surfactants, where k is taken as 0.06. σ increases with increasing hydrophobicity, i.e. the higher the σ value, the more hydrophobic the surfactant.

[0041] EACN is a characteristic of the oily soil to be washed off. Dirty motor oil has for example an EACN value of 8, fresh motor oil of 15 and triglyceride fats (e.g. corn oil, olive oil, soybean oil, sunflower oil and the like) of 16-24. For the purpose of the present invention, a value of 16 can be taken.

[0042] Thus, for the purpose of the present invention a simplified formula for calculating the HLD of a system containing a single surfactant can be used:

$$\text{HLD} = -0.16 \text{ (or } -0.06^*) \times 16 - c_T(T-25) + \sigma$$

* in case of extended surfactants

[0043] Actually, the HLD describes the hydrophilic-lipophilic difference of the entire wash liquor, including the (fatty) soil in the articles to be washed. Since however for the purpose of the present invention the EACN is set at a fixed value (and salinity is not relevant), the properties of the surfactants (especially their relative hydrophilicity/hydrophobicity) at a given temperature are of more significance. Therefore, in a simplified manner, HLD values/properties/profiles are also termed as HLD (values/properties/profiles) of a surfactant or surfactant system or surfactant mixture.

[0044] For determining the HLD of a mixture of different surfactants, the HLD values of the individual surfactants are calculated and the sum of the individual HLD values times the respective molar fraction x_i is formed.

[0045] It was found that the soil cleaning process is dependent on the Hydrophilic-Lipophilic Difference (HLD) profile in the wash liquor. The shifting of the initial HLD from slightly positive or slightly negative to more negative throughout the laundry process (starting roughly from $-3.5 \leq \text{HLD} \leq +1.5$, preferably roughly from $-1 \leq \text{HLD} \leq +0.2$ at the beginning of the wash cycle and arriving at a final HLD of roughly $-5 \leq \text{HLD} \leq -0.5$, preferably at roughly $-4 \leq \text{HLD} \leq -2$ after all of surfactant system S2 has been supplied), where the final HLD value is lower by at least 0.2 than the initial HLD value (i.e. $\text{HLD}_{\text{final}} - \text{HLD}_{\text{initial}} : 5 - 0.2$; or alternatively expressed $\text{HLD}_{\text{initial}} - \text{HLD}_{\text{final}} \geq 0.2$), leads to maximum detergency and minimal redeposition. The initial HLD corresponds to the HLD of the surfactant system S1. If surfactant system S1 consists of a single (hydrophobic) surfactant, the initial HLD corresponds to the HLD of this surfactant. If surfactant system S1 consists of two or more surfactants, the initial HLD is calculated as described above from the HLD of the single surfactants contained in surfactant system S1, i.e. by forming the sum of the individual HLD values in each case multiplied with the respective molar fraction x_i . The final HLD is calculated from the HLD of all surfactants eventually contained in the wash liquor, i.e. all surfactants of surfactant system S1 and all surfactants of surfactant system S2, as described above.

[0046] Thus, preferably the wash liquor applied in step b) has an initial HLD value of -3.5 to +1.5, preferably of -1 to +0.2 and more preferably -1 to +0.1; and the wash liquor obtained in step d), if this is carried out, or obtained in step c), if step d) is not carried out, after surfactant system S2 has been supplied, has a final HLD value of -5 to -0.5, preferably of -5 to -1, more preferably of -4 to -1 or -3 to -1.2, where the final HLD value is lower by at least 0.2 (e.g. by 0.2 to 5 or 0.2 to 4), preferably by at least 0.3 (e.g. 0.3 to 4) and more preferably by at least 1 (e.g. 1 to 4), than the initial HLD value.

[0047] Alternatively expressed, the polarity of the wash liquor is increased during the wash cycle; this is achieved by addition of the surfactant system(s) S2 once or several times or continually.

[0048] Surfactant system S1 comprises one or more hydrophobic surfactants and optionally also one or more hydrophilic surfactants. If S1 also comprises one or more hydrophilic surfactants, their amount is so low that the hydrophobic nature of S1 predominates. Analogously, surfactant system S2 comprises one or more hydrophilic surfactants and optionally also one or more hydrophobic surfactants. If S2 also comprises one or more hydrophobic surfactants, their amount is so low that the hydrophilic nature of S2 predominates.

[0049] Surfactant molecules have both hydrophilic and hydrophobic (lipophilic) groups. In hydrophilic surfactants the influence of the hydrophilic (polar) group predominates; such surfactants show a better water solubility than hydrophobic surfactants and are better for oil-in-water emulsions (O/W). In hydrophobic surfactants the influence of the hydrophobic group predominates; such surfactants show a better solubility in non-polar organic solvents than hydrophilic surfactants and are better for water-in-oil emulsions (W/O). The transition from hydrophilic to hydrophobic is of course fluid; in the present case it is important that the surfactant system S2 be more hydrophilic than the surfactant system S1.

[0050] Hydrophilicity and hydrophobicity of surfactants could be expressed along their HLB values, but HLD is more accurate since it reflects also the influence of temperature thereon.

[0051] In an embodiment, the method of laundering articles of the present invention involves dosing of a surfactant system as defined above and below at defined time intervals of a wash cycle and provides improved detergency of the surfactant system as a result of shifting of HLD towards (more) negative values.

[0052] The present invention is directed to a method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) at point in time T2 (which is of course after T1) supplying the wash liquor of step b), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle, and

d) if desired repeating step c) one or more times.

[0053] Generally, laundering may also comprise:

e) rinsing the laundering articles of the wash liquor, and

f) drying the laundered articles.

[0054] The method of the invention basically corresponds to usual laundering methods, the decisive difference being however that a part or all of the hydrophilic surfactant(s) is supplied only after a certain time.

[0055] Steps a) and b) can, for example, be carried out thusly that in a first step a wash liquor is prepared by dissolving the surfactant system S1 in the liquid medium (generally water) and then the resulting wash liquor is brought into contact with the laundering articles. The wash liquor prepared in the first step may be a concentrate which is further diluted with the liquid medium when or after being brought into contact with the laundering articles, or may be the final, diluted form.

[0056] "Dissolved", "dissolve" and related terms used in the context of the distribution of a surfactant system in a liquid medium are not restricted to the formation of a solution in the proper sense, but are used as a *pars pro toto* term encompassing any form of distribution of the surfactant system in the liquid medium, be it in the form of a true solution, an emulsion, a suspension or a mixed form thereof.

[0057] Alternatively, steps a) and b) can be carried out by preparing the wash liquor *in situ* by either adding the surfactant system S1 and the liquid medium (generally water) simultaneously to the laundering articles or by first soaking the laundering articles in the liquid medium (generally water) and then adding the surfactant system S1 thereto, or by first bringing the surfactant system S1 into contact with the laundering articles and then adding the liquid medium (generally water) thereto.

[0058] The method of the invention can be carried out by usual means for laundering articles, such as hand-washing or

washing in non-automatic or automatic washing machines on household or industrial scale.

[0059] If the method is carried out by hand-washing or washing in non-automatic washing machines, the steps to be taken are auto-explicative: For example, steps a) and b) are carried out as described above, then the washing is initiated and at the desired point in time T2 surfactant system S2 is added. If desired, further (or another) surfactant system S2 is added at a later point in time T3 and washing is continued; if desired this repeated at a later point in time T4 etc.

[0060] The surfactant system S2 used in steps c) and d), respectively, can be the same or different. The difference can lie, for example, in the nature and number of the hydrophilic surfactant(s), in the (relative) amount(s) thereof, in the presence or absence of optionally present hydrophobic surfactant(s), in the nature and the (relative) amount of the latter, in the presence or absence of any further additives, in the nature and the amount of the latter, and the like. Preferably, however, it is the same.

[0061] If the method of the invention is carried out in an automatic washing machine, e.g. in a household or industrial washing machine, steps a) and b) can for example be carried out by first soaking the laundering articles in the liquid medium (generally water) by using the suitable washing program and then adding the surfactant system S1 thereto, which is often carried out by flushing the proper compartment of the detergent drawer with the liquid medium, which then conveys the surfactant system S1 into the washing drum; or by placing the surfactant system S1 along with the laundering articles into the washing drum before the washing machine is started, and then, upon starting, filling in the liquid medium (generally water); or by skipping the soaking step and directly flushing the proper compartment of the detergent drawer with the liquid medium, which then conveys the surfactant system S1 into the washing drum.

[0062] If the method of the invention is carried out in an automatic washing machine, e.g. in a household or industrial washing machine, step c) can for example be carried out by placing surfactant systems 1 and 2 into different compartments of the detergent drawer. The machine has to be conceived or programmed thusly that the compartment in which surfactant system S1 is placed is emptied before the compartment in which surfactant system S2 is placed; where, expediently, the compartment in which surfactant system S2 is placed is emptied at the desired point in time T2.

[0063] Alternatively, and independently of the washing technique (i.e. of whether washing is done by hand or in a non-automatic or automatic washing machine), a surfactant system can be used which contains both surfactant systems 1 and 2, in which at least a part (preferably all) of surfactant system S2 is formulated thusly that its release into the liquid medium is delayed as compared to that of surfactant system S1. An example for such a surfactant system is the formulation of surfactant system S1 and at least a part (preferably all) of surfactant system S2 in separate, individual pods, where the walls of these pods are conceived thusly that the pod containing (at least a part of) surfactant system S2 releases its content into the liquid medium with a time lag after the pod containing surfactant system S1 has released its content. For example, the wall of the pod containing surfactant system S1 is thinner and/or better soluble or degradable in the liquid medium than the wall of the pod containing (at least a part, preferably all, of) surfactant system S2. Another example for such a surfactant system is a detergent pod wherein at least a part (preferably all) of surfactant system S2 is in a compartment within a pod containing surfactant system S1 (and the remainder of surfactant system S2, if applicable) (pod-in-pod system), where the nature or thickness of the wall of said compartment containing (at least a part, preferably all, of) surfactant system S2 is thus that the latter is released from the compartment with a time delay as compared to the release of surfactant system S1. This can be obtained, for instance, by using a wall of the outer pod which is thinner and/or better soluble or degradable in the liquid medium into which the surfactants are to be released (generally water) and a denser and/or less soluble or degradable wall of the inner pod/compartment. Yet another example is a capsule in a capsule with an analogous function. Further details are given in context with the composition of the invention. In case of using such a surfactant system with delayed release of (a part of) surfactant system S2, the point in time T2 is that point in time when the release of surfactant system S2 (to be more precise that part of surfactant system 2 which is formulated to have a delayed release) starts. Said delayed release takes place either more or less abruptly or more or less continuously. In case of a continuous release, distinction between steps c) and d) does not make sense.

[0064] If step d) is carried out once or several times, the surfactant system S2 can be the same as in step c) or different, as already explained above.

[0065] Step d) can be performed analogously to step c).

[0066] Rinsing and drying can be carried out by usual means. In automatic washing machines the rinsing step is included in the wash program.

[0067] In an embodiment, step d) is not carried out. This can be expressed as a method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1, and

c) at point in time T2 (which is of course after T1) supplying the wash liquor of step b), optionally while pausing the wash

cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle.

[0068] Generally, laundering may also comprise:

- e) rinsing the laundering articles of the wash liquor, and
- f) drying the laundered articles.

[0069] In another embodiment the wash cycle is paused in step c), and step d) is not carried out. This can be expressed as a method of laundering articles, the method comprising the steps of:

- a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant,
- b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1, and
- c) pausing the wash cycle and adding a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant to the wash liquor of step b) at point in time T2 (which is of course after T1) and resuming the wash cycle.

[0070] As said above, laundering generally also comprises

- e) rinsing the laundering articles of the wash liquor, and
- f) drying the laundered articles.

[0071] In another embodiment step d) is carried out once. This can be expressed as a method of laundering articles, the method comprising the steps of:

- a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant,
- b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,
- c) at point in time T2 (which is of course after T1) supplying a the wash liquor of step b), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle, and
- d) at point in time T3 (which is of course after T2) supplying the wash liquor of step c), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle.

[0072] As said above, laundering may generally also comprise:

- e) rinsing the laundering articles of the wash liquor, and
- f) drying the laundered articles.

[0073] As said above, the surfactant system S2 used in steps c) and d), respectively, can be the same or different. The difference can lie, for example, in the nature of the hydrophilic surfactant, in the amount thereof, in the presence or absence of optionally present hydrophobic surfactant(s), in the nature and the amount of the latter, in the presence or absence of any further additives, in the nature and the amount of the latter, and the like. Preferably, however, it is the same.

[0074] In another embodiment the wash cycle is paused in step c), and step d) is carried out once. This can be expressed as a method of laundering articles, the method comprising the steps of:

- a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) pausing the wash cycle and adding a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant to the wash liquor of step b) at point in time T2 (which is of course after T1) and resuming the wash cycle, and

d) at point in time T3 (which is of course after T2) supplying the wash liquor of step c), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle.

[0075] As said above, laundering generally also comprises

e) rinsing the laundering articles of the wash liquor, and

f) drying the laundered articles.

[0076] In another embodiment the wash cycle is paused in steps c) and d), and step d) is carried out once. This can be expressed as a method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) pausing the wash cycle and adding a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant to the wash liquor of step b) at point in time T2 (which is of course after T1) and resuming the wash cycle, and

d) pausing the wash cycle and adding a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant to the wash liquor of step b) at point in time T3 (which is of course after T2) and resuming the wash cycle,.

[0077] As said above, laundering generally also comprises

e) rinsing the laundering articles of the wash liquor, and

f) drying the laundered articles.

[0078] In another embodiment, step d) is carried out twice or three times. This can be expressed as a method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) at point in time T2 (which is of course after T1) supplying the wash liquor of step b), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle,

d) at a point in time T3 (which is of course after T2) supplying the wash liquor of step c), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle,

d') at a point in time T4 (which is of course after T3) supplying the wash liquor of step d), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle; and

d'') optionally: at a point in time T5 (which is of course after T4), supplying the wash liquor of step d''), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle.

[0079] As said above, laundering may generally also comprise:

e) rinsing the laundering articles of the wash liquor, and

f) drying the laundered articles.

[0080] The surfactant system S2 used in steps c), d), d') and optionally d''), respectively, can be the same or different. The difference can lie, for example, in the nature of the hydrophilic surfactant, in the amount thereof, in the presence or absence of optionally present hydrophobic surfactant(s), in the nature and the amount of the latter, in the presence or absence of any further additives, in the nature and the amount of the latter, and the like. Preferably, however, it is the same.

[0081] In another embodiment the wash cycle is paused in steps c) and d), and step d) is carried out twice or three times. This can be expressed as a method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) pausing the wash cycle and adding a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant to the wash liquor of step b) at point in time T2 (which is of course after T1) and resuming the wash cycle,

d) pausing the wash cycle and adding a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant to the wash liquor of step c) at point in time T3 (which is of course after T2) and resuming the wash cycle, and

d') pausing the wash cycle and adding a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant to the wash liquor of step d) at point in time T4 (which is of course after T3) and resuming the wash cycle, and

d'') optionally: pausing the wash cycle and adding a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant to the wash liquor of step d') at point in time T5 (which is of course after T4) and resuming the wash cycle.

[0082] As said above, laundering generally also comprises

e) rinsing the laundering articles of the wash liquor, and

f) drying the laundered articles.

[0083] In another embodiment, a surfactant system is used which contains both surfactant systems 1 and 2, in which however at least a part, preferably all, of surfactant system S2 is formulated thusly that its release into the liquid medium is delayed as compared to that of surfactant system S1. In this case the method of the invention can be expressed as a method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S that comprises (1) a surfactant system S1 comprising in turn at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant, and (2) a surfactant system S2 comprising in turn at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, where at least a part, preferably all, of surfactant system S2 is present in a form to delay its release into the liquid medium of the wash liquor as compared to that of surfactant system S1; and

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) where the release of the surfactant system S2 into the wash liquor starts at a point in time T2 which is after T1.

[0084] Steps a) and b) can be carried out in analogy to the proceeding described above. Thus, for example, in a first step a wash liquor is prepared by placing the surfactant system S in the liquid medium (generally water) and then bringing the resulting wash liquor into contact with the laundering articles and starting the wash cycle. The wash liquor may be further diluted with the liquid medium when or after being brought into contact with the laundering articles, if necessary.

Alternatively, steps a) and b) can be carried out by preparing the wash liquor *in situ* by either adding the surfactant system S and the liquid medium (generally water) simultaneously to the laundering articles or by first soaking the laundering articles in the liquid medium (generally water) and then adding the surfactant system S thereto, or by first bringing the surfactant system S into contact with the laundering articles and then adding the liquid medium (generally water) thereto. At least a part, preferably all, of the surfactant system S2 is formulated thusly that its release into the liquid medium is delayed as compared to that of surfactant system S1. Formulations of such a surfactant system S have been described above. More details can also be found below in context with the composition of the invention.

Surfactants:

[0085] The surfactant system S1 used in the method of laundering articles comprises at least one hydrophobic surfactant and optionally also at least one hydrophilic surfactant.

[0086] In an embodiment, the surfactant system S1 comprises two hydrophobic surfactants and 1 hydrophilic surfactant.

[0087] In another embodiment, the surfactant system S1 comprises two hydrophobic surfactants and no hydrophilic surfactant.

[0088] In another embodiment, the surfactant system S1 comprises three or more hydrophobic surfactants and 1 hydrophilic surfactant.

[0089] In another embodiment, the surfactant system S1 comprises three or more hydrophobic surfactants and no hydrophilic surfactant.

Among the above, preference is given to a surfactant system S1 comprising two or three, preferably two, hydrophobic surfactants and no or one hydrophilic surfactant.

[0091] The surfactant system S2 (also in form of S2', S2'', S2''' ..) used in the method of laundering articles comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant.

[0092] In an embodiment, the surfactant system S2 comprises two hydrophilic surfactants and 1 hydrophobic surfactant.

[0093] In another embodiment, the surfactant system S2 comprises three or more hydrophilic surfactants and 1 hydrophobic surfactant.

[0094] In another embodiment, the surfactant system S2 comprises two hydrophilic surfactants and no hydrophobic surfactant.

[0095] In another embodiment, the surfactant system S2 comprises one hydrophilic surfactant and no hydrophobic surfactant.

Among the above, preference is given to a surfactant system S2 comprising one hydrophilic surfactant and no hydrophobic surfactant.

[0097] Specifically, the surfactant system S1 comprises two hydrophobic surfactants and no or one hydrophilic surfactant, and the surfactant system S2 comprises one hydrophilic surfactant and no hydrophobic surfactant.

[0098] The weight ratio of the overall amount of hydrophobic surfactant(s) (as comprised in surfactant system 1 and, if applicable, in surfactant system 2) to the overall amount of hydrophilic surfactant(s) (as comprised in surfactant system 2 and, if applicable, in surfactant system 1) is preferably in the range of 5:1 to 1:5, more preferably from 3:1 to 1:1.5, in particular from 3:1 to 1:1 and specifically from 2:1 to 1:1.

[0099] In the method of the invention the surfactants contained in surfactant systems 1 and 2 can be used in a total amount which corresponds to the amounts in which surfactants are typically dosed in washing processes. Since however the washing performance is higher when the method of the invention is applied, the dosage can also be lower.

[0100] In an embodiment, the surfactants are selected from compounds of formula (I), R



wherein

R₁ is selected from linear or branched C₄-C₂₂ alkyl,

R₂ is selected from H and linear or branched C₁-C₂₂ alkyl,

A is CH₂-CH₂-O,

B is CH₂-CHR₃-O, wherein R₃ is linear or branched C₁-C₁₀ alkyl,

x is in the range from 0 to 35,

y1 is in the range from 0 to 60,
 y2 is in the range from 0 to 35,
 z is in the range from 0 to 35, and

5 wherein the sum of $x+y_1+z+y_2$ is at least 2;

[0101] In an embodiment, the compound of formula (I) is a hydrophobic surfactant.

[0102] In another embodiment, the compound of formula (I) is a hydrophilic surfactant. More details are given below.

[0103] In an embodiment, in the compound of formula (I), x or y1 or z or y2 is in the range of 0 to 20.

10 **[0104]** Preferably the sum of $x+y_1+z+y_2$ is in the range of 2 to 50, more preferably the sum of $x+y_1+z+y_2$ is in the range of 2 to 40 even more preferably the sum of $x+y_1+z+y_2$ is in the range of 2 to 30 and most preferably the sum of $x+y_1+z+y_2$ is in the range of 2 to 25. Specifically, the sum of $x+y_1+z+y_2$ is in the range of 2 to 20, and more specifically in the range of 3 to 15.

[0105] Preferably, R₁ is linear or branched C₈-C₁₆ alkyl, more preferably linear or branched C₁₀-C₁₆ alkyl.

[0106] Preferably, R₂ is hydrogen.

[0107] Preferably, R₃ is methyl.

15 **[0108]** In an embodiment, in the compound of formula (I), R₁ is linear or branched C₁₀-C₁₆ alkyl, x = is 2 to 8, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0109] In a preferred embodiment x + z = 2-5, preferably 3-5, and y₁ and y₂ = 0. More preferably, x + z = 2-5, preferably 3-5, y₁ and y₂ = 0, and R₂ is hydrogen. Alternatively expressed, preferably x = 2-5, preferably 3-5, and y₁, y₂ and z = 0. More preferably, x = 2-5, preferably 3-5, y₁, y₂ and z = 0, and R₂ is hydrogen. In this context, too, R₁ is preferably linear or

20 branched C₁₀-C₁₆ alkyl.

[0110] In another preferred embodiment, x + z = 6-10, preferably 7-8, specifically 7, and y₁ and y₂ = 0. More preferably, x + z = 6-10, preferably 7-8, specifically 7, y₁ and y₂ = 0, and R₂ is hydrogen. Alternatively expressed, preferably x = 6-10, preferably 7-8, specifically 7, and y₁, y₂ and z = 0. More preferably, x = 6-10, preferably 7-8, specifically 7, y₁, y₂ and z = 0, and R₂ is hydrogen. In this context, too, R₁ is preferably linear or branched C₁₀-C₁₆ alkyl.

25 **[0111]** In yet another preferred embodiment, x+z = 3-8, specifically 4-7, y₁+y₂ = 6 to 10, specifically 8, and R₃ is methyl. More preferably, x+z = 3-8, specifically 4-7, y₁+y₂ = 6 to 10, specifically 8, R₃ is methyl and R₂ is hydrogen. In particular, x is 0, y₁ is 6 to 10, specifically 8, y₂ is 0, z is 3-8, specifically 4-7, and R₃ is methyl. More particularly, x is 0, y₁ is 6 to 10, specifically 8, y₂ is 0, z is 3-8, specifically 4-7, R₃ is methyl and R₂ is hydrogen. In this context, too, R₁ is preferably linear or branched C₁₀-C₁₆ alkyl.

30 **[0112]** In a preferred embodiment, R₁ is branched C₁₃ alkyl, x = is 2-4, specifically 3, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0113] In an embodiment, in the compound of formula (I), R₁ is linear or branched C₁₀-C₁₆ alkyl, x = is 4 to 10, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0114] In a preferred embodiment, R₁ is branched C₁₃-C₁₅ alkyl, x = is 4 to 8, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

35 **[0115]** In an embodiment, in the compound of formula (I), R₁ is linear or branched C₁₀-C₁₆ alkyl, x = is 2 to 8, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0116] In a preferred embodiment, R₁ is branched C₁₃-C₁₅ alkyl, x = is 2 to 6, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0117] In an embodiment, in the compound of formula (I), R₁ is linear or branched C₁₀-C₁₆ alkyl, x = is 4 to 10, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0118] In a preferred embodiment, R₁ is branched C₁₃-C₁₅ alkyl, x = is 4 to 7, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

40 **[0119]** In an embodiment, in the compound of formula (I), R₁ is linear or branched C₁₀-C₁₆ alkyl, x = is 2 to 10, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0120] In a preferred embodiment, R₁ is branched C₁₃-C₁₅ alkyl, x = is 2-8, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0121] In an embodiment, in the compound of formula (I), R₁ is linear C₁₂-C₁₄ alkyl, x = is 4-7, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

45 **[0122]** In an embodiment, in the compound of formula (I), R₁ is linear C₁₂-C₁₄ alkyl, x = is 7, y₁ = 0, z = 0, y₂ = 0, and R₂ is H.

[0123] In an embodiment, in the compound of formula (I), R₁ is branched C₈-C₁₄ alkyl, x = is 0, y₁ = 6-10, z = 6-10, y₂ = 0, and R₂ is H.

50 **[0124]** In a preferred embodiment, in the compound of formula (I), R₁ is branched C₁₀ alkyl, x = is 0, y₁ = 8, z = 7, y₂ = 0, and R₂ is H.

[0125] In an embodiment, in the compound of formula (I), R₁ is branched C₈-C₁₄ alkyl, x = is 0, y₁ = 6-10, z = 2-6, y₂ = 0, and R₂ is H.

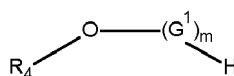
[0126] In a preferred embodiment, R₁ is branched C₁₀ alkyl, x = is 0, y₁ = 8, z = 4, y₂ = 0, and R₂ is H.

55 **[0127]** In an embodiment, in the compound of formula (I), the moiety R₁O is derived from a linear or branched C₄ to C₁₈ alkanol, preferably from a C₈ to C₁₈ alkanol, where the alkanol is in particular selected from 2-propylheptanol, lauryl alcohol, linear or branched tridecyl alcohol, myristyl alcohol, C₁₃-C₁₅ oxo alcohols and mixtures thereof.

[0128] The degrees of alkoxylation/ethoxylation stated in context with compounds (I) as well as with compounds (IV) described below are statistical averages which, for a specific product, may be an integer or a fraction. For instance, in an

ethoxylated alkanol molecule containing 3 units of ethylene oxide, "on average" means that some of the ethoxylated alkanol molecules may contain more than 3 EO units and some may contain less than 3 EO units, the average number of repeat units being however 3.

[0129] In another embodiment, the surfactants are selected from compounds of formula (II),



Compound of formula (II),

wherein

R_4 is a linear or branched C_6 to C_{30} alkyl,

G^1 is a monosaccharide residue having 5 or 6 carbon atoms, and

m is on average in the range of 1 to 10.

[0130] In an embodiment, the compound of formula (II) is hydrophobic surfactant.

[0131] As used herein, the term "branched alkyl" is denotes an alkyl radical having an average number of branching of at least 0.7 as defined below. Preferably, the term "branched alkyl" refers to a radical of a saturated branched aliphatic group having an average number of branching of ranging from 0.9 to 3.5, more preferably ranging from 1.8 to 3.5 and most preferably from 2.0 to 2.5 as defined below. It is appreciated that the number of carbon atoms includes carbon atoms along the chain backbone as well as branching carbons.

[0132] As used herein, 'average number of branches per molecule chain' refers to the average number of branches per alcohol molecule which corresponds to the corresponding branched alkyl, as measured by ^{13}C Nuclear Magnetic Resonance (^{13}C NMR). The average number of carbon atoms in the chain are determined by gas chromatography.

[0133] Various references will be made throughout this specification and the claims to the percentage of branching at a given carbon position, the percentage of branching based on types of branches, the average number of branches and the percentage of quaternary atoms. These amounts are to be measured and determined by using a combination of the following three ^{13}C -NMR techniques.

[0134] (1) The first is the standard inverse gated technique using a 45-degree tip ^{13}C pulse and 10 s recycle delay (an organic free radical relaxation agent is added to the solution of the branched alcohol in deuterated chloroform to ensure quantitative results). (2) The second is a J-Modulated Spin Echo NMR technique (JMSE) using a $1/J$ delay of 8 ms (J is the 125 Hz coupling constant between carbon and proton for these aliphatic alcohols). This sequence distinguishes carbons with an odd number of protons from those bearing an even number of protons, i.e. CH_3/CH vs CH_2/Cq (Cq refers to a quaternary carbon) (3) The third is the JMSE NMR "quat-only" technique using a $1/2 J$ delay of 4 ms which yields a spectrum that contains signals from quaternary carbons only. The JSME NMR quat only technique for detecting quaternary carbon atoms is sensitive enough to detect the presence of as little as 0.3 atom % of quaternary carbon atoms. As an optional further step, if one desires to confirm a conclusion reached from the results of a quat only JSME NMR spectrum, one may also run a DEPT-135 NMR sequence. The DEPT-135 NMR sequence may be very helpful in differentiating true quaternary carbons from breakthrough protonated carbons. This is due to the fact that the DEPT-135 sequence produces the "opposite" spectrum to that of the JMSE "quat-only" experiment. Whereas the latter nulls all signals except for quaternary carbons, the DEPT-135 nulls exclusively quaternary carbons. The combination of the two spectra is therefore very useful in spotting non quaternary carbons in the JMSE "quat only" spectrum. When referring to the presence or absence of quaternary carbon atoms throughout this specification, however, it is meant that the given amount or absence of the quaternary carbon is as measured by the quat only JSME NMR method. If one optionally desires to confirm the results, then also using the DEPT-135 technique to confirm the presence and amount of a quaternary carbon.

[0135] For example, the branched C_{13} -alkyl has an average number of branching of from 0.9 to 3.5, more preferably ranging from 1.8 to 3.5 and most preferably from 2.0 to 2.5. The number of branching is defined as the number of methyl groups in one molecule of the corresponding alcohol of the branched alkyl minus 1. The average number of branching is the statistical average of the number of branching of the molecules of a sample.

[0136] The branched alkyl can be characterized by the NMR technique as having from 5 to 25 % branching on the C_2 carbon position, relative to the ether group. In a preferred embodiment, from 10 to 20% of the number of branches are at the C_2 position, as determined by the NMR technique. The branched alkyl also generally has from 10% to 50% of the number of branches on the C_3 position, more typically from 15% to 30 % on the C_3 position, also as determined by the NMR technique.

When coupled with the number of branches seen at the C₂ position, the branched alkyl in this case contains a significant amount of branching at the C₂ and C₃ carbon positions.

[0137] Thus, the branched alkyl of the present invention has a significant number of branches at the C₂ and C₃ positions. Additionally, or alternatively, the branched alkyl preferably has $\geq 7\%$, more preferably $\leq 5\%$ of isopropyl terminal type of branching, as determined by the NMR technique, meaning methyl branches at the second to last carbon position in the backbone relative to the ether group.

[0138] In one embodiment, the branching occurs across the length of the carbon backbone. It is however preferred that at least 20 %, more preferably at least 30 %, of the branches are concentrated at the C₂, C₃, and isopropyl positions. Alternatively, the total number of methyl branches number is at least 40 %, even at least 50 %, of the total number of branches, as measured by the NMR technique described above. This percentage includes the overall number of methyl branches seen by the NMR technique described above within the C₁ to the C₃ carbon positions relative to the ether group, and the terminal isopropyl type of methyl branches.

[0139] In one embodiment, the surfactant (II) is a mixture of two or more different compounds (II). In one embodiment, the two or more compounds of the composition differ in R₄. Preferably, the composition comprises a mixture of two or more compounds of the general formula (II) differing in R₄, while G¹ and m are the same. If two or more compounds of the composition differ in R₄, R₄ may differ in the number of carbon atoms (i.e. the length) or the kind of branching.

[0140] For example, if the two or more compounds of the composition differ in the number of carbon atoms (i.e. the length), one of the two or more compounds is a compound, wherein R₄ is unsubstituted branched C₉-alkyl, and one or more compound(s) of the two or more compounds is a compound, wherein R₄ is unsubstituted branched C₁₀-alkyl, unsubstituted branched C₁₁-alkyl, unsubstituted branched C₁₂-alkyl and/or unsubstituted branched C₁₃-alkyl.

[0141] Alternatively, if the two or more compounds of the composition differ in the kind of branching, it is appreciated that the two or more compounds are compounds having the same number of carbon atoms (i.e. the length), but the branching across the length of the carbon backbone is different. For example, each of the two or more compounds are unsubstituted branched C₁₃-alkyl, wherein R₄ differs in the branching across the length of the carbon backbone. Accordingly, R₄ is a mixture of different branched C₉-C₁₃-alkyl.

[0142] If R₄ is a mixture of different branched C₉-C₁₅ alkyl, it is appreciated that it is not excluded that the composition comprises minor amounts of R₄ being straight-chain C₉-C₁₅ alkyl, i.e. C₉-C₁₅ alkyl being free of branches. For example, the composition comprising two or more compounds of the general formula (II), comprises one or more compounds, wherein R₄ is straight-chain C₉-C₁₅ alkyl, in an amount of ≥ 1.0 wt.-%, based on the total weight of the composition.

[0143] Preferably, the two or more compounds of the composition differ in R₄.

[0144] The two or more compounds of the general formula (II) which differ in R₄ are preferably obtained by the corresponding glycosylation of a mixture of alcohols. Such alcohol mixtures are typically technical mixtures obtained in industrial processes. Preferably the alcohol mixture is one obtained by hydroformylating and optionally hydrogenation of a trimer butene or a tetramer propene, more preferably of a trimer butene. A process for preparing the mixture of alcohols is e.g. described in WO 2001/36356 A2.

[0145] In the general formula (II), G¹ is selected from monosaccharides with 5 or 6 carbon atoms. For example, G¹ is selected from pentoses and hexoses. Examples of pentoses are ribulose, xylulose, ribose, arabinose, xylose and lyxose. Examples of hexoses are galactose, mannose, rhamnose and glucose. Monosaccharides may be synthetic or derived or isolated from natural products, hereinafter in brief referred to as natural saccharides or natural polysaccharides, and natural saccharides natural polysaccharides being preferred. More preferred are the following natural monosaccharides: glucose, xylose, arabinose, rhamnose and mixtures of the foregoing, even more preferred are glucose and/or xylose, and in particular xylose. Monosaccharides can be selected from any of their enantiomers, naturally occurring enantiomers and naturally occurring mixtures of enantiomers being preferred. Naturally, in a specific molecule, only whole groups of G¹ can occur.

[0146] Thus, if G¹ in the general formula (II) is a pentose, the pentose may be selected from ribulose such as D-ribulose, L-ribulose and mixtures thereof, preferably D-ribulose, xylulose such as D-xylulose, L-xylulose and mixtures thereof, preferably D-xylulose, ribose such as D-ribose, L-ribose and mixtures thereof, preferably D-ribose, arabinose such as D-arabinose, L-arabinose and mixtures thereof, preferably L-arabinose, xylose such as D-xylose, L-xylose and mixtures thereof, preferably D-xylose and lyxose such as D-lyxose, L-lyxose and mixtures thereof, preferably D-lyxose. If G¹ in the general formula (II) is a hexose, the hexose may be selected from galactose such as D-galactose, L-galactose and mixtures thereof, preferably D-galactose, mannose such as D-mannose, L-mannose and mixtures thereof, preferably D-mannose, rhamnose such as D-rhamnose, L-rhamnose and mixtures thereof, preferably L-rhamnose and glucose such as D-glucose, L-glucose and mixtures thereof, preferably D-glucose. More preferably, G¹ in the general formula (II) is glucose, preferably D-glucose, xylose, preferably D-xylose, arabinose, preferably D-arabinose, rhamnose, preferably L-rhamnose, and mixtures of the foregoing, even more preferably G¹ in the general formula (II) is glucose, preferably D-glucose and/or xylose, preferably D-xylose, and/or arabinose, preferably D-arabinose, and in particular xylose, preferably D-xylose and/or arabinose, preferably D-arabinose. For example, G¹ in the general formula (II) is xylose, preferably D-xylose or arabinose, preferably D-arabinose.

[0147] In one embodiment, G^1 is selected from monosaccharides with 5 or 6 carbon atoms, which are obtained from a fermentative process of a biomass source. The biomass source may be selected from the group comprising pine wood, beech wood, wheat straw, corn straw, switchgrass, flax, barley husk, oat husk, bagasse, miscanthus and the like.

[0148] Thus, it is appreciated that G^1 can comprise a mixture of monosaccharides with 5 or 6 carbon atoms.

[0149] Accordingly, in another preferred embodiment, the surfactant (II) is a mixture of two or more different compounds (II), where the two or more compounds differ in G^1 (and may additionally differ in R_4 as well).

[0150] Preferred mixtures of monosaccharides with 5 or 6 carbon atoms include, but are not limited to, a mixture of xylose and glucose or a mixture of xylose and arabinose and optionally glucose. Thus, G^1 is preferably a mixture of xylose and glucose or a mixture of xylose and arabinose and optionally glucose.

[0151] If the mixture of monosaccharides with 5 or 6 carbon atoms comprises a mixture of glucose and xylose, the weight ratio of glucose to xylose may vary in a wide range, depending on the biomass source used. For example, if the mixture of monosaccharides with 5 or 6 carbon atoms comprises a mixture of glucose and xylose, the weight ratio of glucose to xylose (glucose [wt.-%]/xylose [wt.-%]) in the mixture is preferably from 20:1 to 1:10, more preferably from 10:1 to 1:5, even more preferably from 5:1 to 1:2 and most preferably from 3:1 to 1:1.

[0152] If the mixture of monosaccharides with 5 or 6 carbon atoms comprises a mixture of xylose and arabinose, the weight ratio of xylose to arabinose may vary in a wide range, depending on the biomass source used. For example, if the mixture of monosaccharides with 5 or 6 carbon atoms comprises a mixture of xylose and arabinose, the weight ratio of xylose to arabinose (xylose [wt.-%]/arabinose [wt.-%]) in the mixture is preferably from 150:1 to 1:10, more preferably from 100:1 to 1:5, even more preferably from 90:1 to 1:2 and most preferably from 80:1 to 1:1.

[0153] If the mixture of monosaccharides with 5 or 6 carbon atoms comprises a mixture of glucose and xylose and arabinose, the weight ratio of glucose to xylose to arabinose may vary in a wide range, depending on the biomass source used. For example, if the mixture of monosaccharides with 5 or 6 carbon atoms comprises a mixture of glucose and xylose and arabinose, the weight ratio of glucose to arabinose (glucose [wt.-%]/arabinose [wt.-%]) in the mixture is preferably from 220:1 to 1:20, more preferably from 200:1 to 1:15, even more preferably from 190:1 to 1:10 and most preferably from 180:1 to 1:8. Additionally or alternatively, the weight ratio of xylose to arabinose (xylose [wt.-%]/arabinose [wt.-%]) in the mixture is preferably from 150:1 to 1:20, more preferably from 120:1 to 1:15, even more preferably from 100:1 to 1:10 and most preferably from 80:1 to 1:8. Additionally or alternatively, the weight ratio of glucose to xylose (glucose [wt.-%]/xylose [wt.-%]) in the mixture is preferably from 150:1 to 1:20, more preferably from 120:1 to 1:15, even more preferably from 100:1 to 1:10 and most preferably from 80:1 to 1:8.

[0154] In one embodiment, especially if G^1 is obtained from a fermentative process of a biomass source, G^1 may comprise minor amounts of monosaccharides differing from the monosaccharides with 5 or 6 carbon atoms.

[0155] Preferably, G^1 comprises ≤ 10 wt.-%, more preferably ≤ 5 wt.-%, based on the total weight of the monosaccharide, of monosaccharides differing from the monosaccharides with 5 or 6 carbon atoms. That is to say, G^1 comprises ≥ 90 wt.-%, more preferably ≥ 95 wt.-%, based on the total weight of the monosaccharide, of the monosaccharides with 5 or 6 carbon atoms.

[0156] In the general formula (II), m (also named degree of polymerization (DP)) is in the range of from 1 to 10, preferably m is in the range of from 1.05 to 2.5 and most preferably m is in the range of from 1.10 to 1.8, e.g. from 1.1 to 1.4. In the context of the present invention, m refers to average values, and m is not necessarily a whole number. In a specific molecule only whole groups of G^1 can occur. It is preferred to determine m by high temperature gas chromatography (HTGC), e.g. 400° C, in accordance with K. Hill et al., Alkyl Polyglycosides, VCH Weinheim, New York, Basel, Cambridge, Tokyo, 1997, in particular, pages 28 ff., or by HPLC. In HPLC methods, m may be determined by the Flory method. If the values obtained by HPLC and HTGC are different, preference is given to the values based on HTGC. In an embodiment, G^1 is selected from glucose, xylose, arabinose, rhamnose, and mixtures thereof.

[0157] It is appreciated that the compounds of the general formula (II) can be present in the alpha and/or beta conformation. For example, the compound of general formula (II) is in the alpha or beta conformation, preferably alpha conformation. Alternatively, the compound of general formula (II) is in the alpha and beta conformation.

[0158] If the compound of general formula (II) is in the alpha and beta conformation, the compound of general formula (II) comprises the alpha and beta conformation preferably in a molar ratio (α/β) from 10:1 to 1:10, more preferably from 10:1 to 1:5, even more preferably from 10:1 to 1:4 and most preferably from 10:1 to 1:3, e.g. about 2:1 to 1:2. In an embodiment, m is in the range of 1.05 to 2.5.

[0159] In an embodiment, R_4 is a linear or branched C_6 to C_{20} alkyl.

[0160] In a preferred embodiment, R_4 is a linear C_8 to C_{14} alkyl.

[0161] In a more preferred embodiment, R_4 is a linear C_8 to C_{12} alkyl.

[0162] In an embodiment, R_4 is a branched C_9 to C_{15} alkyl.

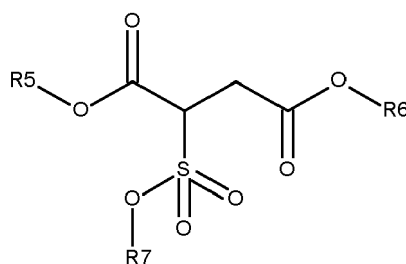
[0163] In a preferred embodiment, R_4 is a branched C_9 to C_{13} alkyl.

[0164] In a more preferred embodiment, R_4 is a branched C_9 or C_{10} or C_{13} alkyl.

[0165] In a most preferred embodiment, R_4 is a linear C_{12} alkyl or a linear or branched C_{10} or C_{13} alkyl.

[0166] In a most preferred embodiment, m is in the range of 1.1 to 1.8.

[0167] In yet another embodiment, the surfactants are selected from compounds of formula (III),



Compound of formula (III),

wherein, each of R_5 and R_6 is independently a linear or branched C_4 - C_{22} alkyl or a linear or branched unsaturated aliphatic C_4 - C_{22} hydrocarbon radical, and R_7 is a hydrogen atom or alkali metal or an alkaline earth metal cation equivalent.

[0168] In case R_7 is an alkali metal or an alkaline earth metal cation equivalent, the sulfonate group should more accurately be depicted in the salt form as $-S(=O)_2O^- (R_7^{m+})_{1/m}$, where m is 1 (if R_7 is an alkali metal, to be more precise an alkali metal cation) or 2 (if R_7 is an alkaline earth metal equivalent, to be more precise an alkaline earth metal cation equivalent $(R_7^{2+})_{1/2}$). Suitable alkali metal cations are Li^+ , Na^+ , K^+ and Cs^+ , preference being given to Na^+ and K^+ and specifically to Na^+ . Suitable alkaline earth metal cations are Mg^{2+} and Ca^{2+} .

[0169] Preferably, R_5 and R_6 are independently of each other linear or branched C_4 - C_{22} alkyl.

[0170] In an embodiment, the compound of formula (III) is hydrophobic surfactant.

[0171] In another embodiment, the compound of formula (III) is hydrophilic surfactant.

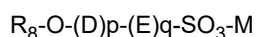
[0172] In an embodiment, in the compound of formula (III), each of R_5 and R_6 is independently a linear or branched C_6 - C_{20} alkyl or a linear or branched unsaturated aliphatic C_6 - C_{20} hydrocarbon radical.

[0173] In another embodiment, in the compound of formula (III), each of R_5 and R_6 is independently a linear or branched C_6 - C_{12} alkyl or a linear or branched unsaturated aliphatic C_6 - C_{12} hydrocarbon radical. More preferably, each of R_5 and R_6 is independently a linear or branched C_6 - C_{12} alkyl, in particular a linear or branched C_6 - C_{10} alkyl and more particularly a linear or branched C_8 - C_{10} alkyl.

[0174] In a preferred embodiment, in the compound of formula (III), each of R_5 and R_6 is independently a linear or branched C_8 alkyl or a linear or branched unsaturated aliphatic C_8 -hydrocarbon radical. More preferably, each of R_5 and R_6 is independently a linear or branched C_8 alkyl.

[0175] In a preferred embodiment, in the compound of formula (III), R_7 is an alkali metal or an alkaline earth metal cation equivalent, more preferably an alkali metal (cation).

[0176] In an embodiment, the surfactants are selected from compounds of formula (IV)



Compound of formula (IV)

wherein

R_8 is a linear or branched C_6 - C_{22} alkyl,

D denotes $CH_2-CH(R_9)-O$, wherein R_9 is linear or branched C_1 - C_{10} alkyl, preferably methyl,

E denotes CH_2-CH_2-O ,

p is in the range from 0 to 10,

q is in the range from 0 to 5,

M is H or an alkali metal or ammonium cation.

[0177] In case M is an alkali metal or ammonium cation, the sulfonate group should more accurately be depicted in the salt form as $-S(=O)_2O^- M^+$. Suitable alkali metal cations are Li^+ , Na^+ , K^+ and Cs^+ , preference being given to Na^+ and K^+ and specifically to Na^+ . Ammonium in this context refers to the ammonium cation NH_4^+ in the proper sense.

[0178] In an embodiment, in the compound of formula (IV), R_8 is linear or branched C_{10} - C_{16} alkyl, $p = 0$ to 8, $q = 0$ to 6, $M =$ alkali metal cation, and the sum of $p+q$ is at least 2.

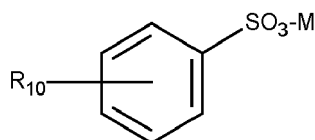
[0179] In a preferred embodiment, in the compound of formula (IV), R_8 is linear or branched C_{10} - C_{14} alkyl, p is 0, q is 2 to 4, and M is an alkali metal cation.

[0180] In a more preferred embodiment, in the compound of formula (IV), R_8 is linear or branched C_{12} alkyl, $p = 0$, $q = 3$, and $M = \text{sodium}$.

[0181] In an embodiment, the compound of formula (IV) is a hydrophilic surfactant.

[0182] In an embodiment, the surfactants are selected from compounds (V) which are selected from C_5 - C_{20} alkylbenzene sulfonic acids and salts thereof.

[0183] Such compounds can be depicted by following formula (V):

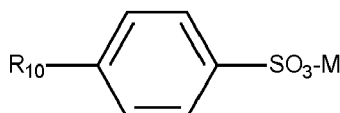


(V)

where R_{10} is C_5 - C_{20} -alkyl and M is hydrogen or an alkali metal or ammonium cation.

[0184] In case M is an alkali metal or ammonium cation, the sulfonate group should more accurately be depicted in the salt form as $-S(=O)_2O^- M^+$. Suitable alkali metal cations are Li^+ , Na^+ , K^+ and Cs^+ , preference being given to Na^+ and K^+ and specifically to Na^+ . Ammonium in this context refers to the ammonium cation NH_4^+ in the proper sense.

[0185] Preferably, R_{10} is in para-position to the sulfonic acid/sulfonate group, such compounds having the formula (V.1):



(V.1)

[0186] In an embodiment, the surfactants are selected from compounds (V) or (V.1) which are selected from C_5 - C_{15} alkylbenzene sulfonic acids and salts thereof (i.e. R_{10} is C_5 - C_{15} -alkyl).

[0187] In a preferred embodiment, the surfactant (V) or (V.1) is a C_{10} - C_{14} alkylbenzene sulfonic acid or a salt thereof (i.e. R_{10} is C_{10} - C_{14} -alkyl), e.g. a C_{12} -alkyl-benzene sulfonic acid or a salt thereof (i.e. R_{10} is C_{12} -alkyl).

[0188] In an embodiment, the compound of formula (V) (or V.1) is a hydrophilic surfactant.

[0189] Compounds (I) to (V) are generally commercially available. Just by way of example, compounds (I) are available under the Lutensol® and Plurafac® brands of BASF; compounds (II) are available under the Glucocon® and APG® brands of BASF; compounds (III) are available under the Lutensit® brand of BASF; compounds (IV) are available under the Sensapol® and Kopacol® brands of Kensing; and compounds (V) are available under the BIO-SOFT® brand of Stepan. If specific compounds (I) to (V) are not commercially available, these can be prepared by standard reactions in organic chemistry, e.g. in analogy to the preparation methods for the commercial products. For instance, compounds (I) wherein R_2 is H can be prepared by reacting an alcohol R_1 -OH with the desired alkoxide, e.g. with ethylene oxide (if at least one of x and z is not 0) and/or with at least one higher alkoxide



where R_3 is as defined above (if at least one of y_1 and y_2 is not 0). To obtain compounds (I) wherein R_2 is alkyl, the alkoxylated alcohol can for example be further reacted with an alcohol R_2 -OH or a more reactive derivative thereof, such as the corresponding chloride or sulfonate, e.g. the triflate or tosylate. Compounds (II) can be prepared by etherifying a suitable mono- or oligosaccharide. Compounds (III) can be prepared by esterification of the commercially available sulfosuccinic acid. Compounds (IV) can be prepared by sulfonating a suitably alkoxylated alcohol (obtainable as described above for compounds (I)). Compounds (V) can be prepared by reacting an alkylbenzene with a sulfonating agent. The alkyl benzene is in turn obtainable by Friedel Crafts alkylation or by reaction of benzene with an olefine.

[0190] The hydrophilic and hydrophobic surfactants can be based on the same structures. Whether they are rather hydrophobic or rather hydrophilic depends mainly on the nature of the polar moiety, but also on the nature and especially the size (chain length) of the non-polar part.

[0191] Thus among the above structures (I) to (V), the hydrophobic surfactant is preferably selected from the group consisting of:

a) at least one compound of formula (I), wherein

- $(y_1 + y_2) = 0$ and $(x + z) \leq 5$, preferably 3 to 5; or
- $(x + z) = 0$; or
- $(y_1 + y_2) \neq 0$, $(x + z) \neq 0$ and $(x+z) - (y_1 + y_2) \leq 2$; preferably ≤ 0 ; or
- R_2 is linear or branched C_1 - C_{22} alkyl;

where the last condition (R_2 is linear or branched C_1 - C_{22} alkyl) can apply simultaneously with one or more of the first three conditions;

b) at least one compound of formula (II); and

c) at least one compound of formula (III), wherein R_5 and R_6 have together at least 14 carbon atoms.

[0192] Among the above structures (I) to (V), the hydrophilic surfactant is preferably selected from the group consisting of:

a) at least one compound of formula (I), wherein

- $(y_1 + y_2) < 3$ and $(x + z) \geq 6$, preferably ≥ 6.5 , e.g. 6.5 to 10 or 7 to 10; and R_2 is hydrogen;

c) at least one compound of formula (III), wherein R_5 and R_6 have together at most 12 carbon atoms; wherein preferably R_7 is an alkali metal or an alkaline earth metal cation (equivalent);

d) at least one compound of formula (IV), wherein M is preferably an alkali metal or ammonium cation; and

e) at least one compound of formula (V), which is preferably a salt of a C_5 - C_{20} alkylbenzene sulfonic acid.

[0193] Irrespective of whether the compound (I) is a hydrophobic or a hydrophilic surfactant, the above preferred definitions of R_1 apply here, too. Thus, R_1 is preferably linear or branched C_8 - C_{16} alkyl, more preferably linear or branched C_{10} - C_{16} alkyl.

[0194] In preferred hydrophobic compounds (I), $(y_1 + y_2) = 0$ and $(x + z) \leq 5$, preferably 3 to 5. In alternatively preferred hydrophobic compounds (I), $x+z = 3-8$, specifically 4-7, $y_1+y_2 = 6$ to 10, specifically 8, and R_3 is methyl. More preferably, $x+z = 3-8$, specifically 4-7, $y_1+y_2 = 6$ to 10, specifically 8, R_3 is methyl and R_2 is hydrogen. In particular, x is 0, y_1 is 6 to 10, specifically 8, y_2 is 0, z is 3-8, specifically 4-7, and R_3 is methyl. More particularly, x is 0, y_1 is 6 to 10, specifically 8, y_2 is 0, z is 3-8, specifically 4-7, R_3 is methyl and R_2 is hydrogen.

[0195] In preferred hydrophilic compounds (I), $(y_1 + y_2) = 0$ and $(x + z) > 6$, more preferably ≥ 6.5 , e.g. 6.5 to 10 or 7 to 10. R_2 is hydrogen, as defined above.

[0196] Preferred compounds (II) have been described above.

[0197] Irrespective of whether the compound (III) is a hydrophobic or a hydrophilic surfactant, R_7 is preferably an alkali metal cation, more preferably a Na or K cation, specifically a Na cation.

[0198] Preferably, compound (III) is used as a hydrophobic surfactant, R_5 and R_6 thus having together at least 14 carbon atoms. Preferably R_5 and R_6 are independently of each other C_6 - C_{10} -alkyl, provided they have together at least 14 carbon atoms, preferably at least 16 carbon atoms, e.g. 16 to 18 carbon atoms.

[0199] Preferred compounds (IV) and (V) have been described above.

[0200] The surfactant system S1 can comprise just one surfactant, namely just a hydrophobic surfactant, but more often comprises two or more different surfactants, e.g. 2, 3 or 4 different surfactants, preferably 2, 3 or 4 hydrophobic surfactants, and optionally also 1 or 2 hydrophilic surfactants. Preferably, the surfactant system S1 comprises two or three, preferably two, different hydrophobic surfactants and no or one hydrophilic surfactant.

[0201] The surfactant system S2 can comprise just one surfactant, namely just a hydrophilic surfactant, or can comprise two or more different surfactants, e.g. 2, 3 or 4 different surfactants, preferably 2, 3 or 4 hydrophilic surfactants. The surfactant system S2 may also comprise 1 or 2 hydrophobic surfactants, but more often comprises only one or more

hydrophilic surfactants. Preferably, the surfactant system S2 comprises one or two different hydrophilic surfactants and no hydrophobic surfactant. More preferably, the surfactant system S2 comprises one hydrophilic surfactant and no hydrophobic surfactant.

[0202] The systems S1 and S2 can moreover comprise one or more "intermediate" surfactants, i.e. surfactants which are neither typically hydrophilic nor typically hydrophobic. Examples of such intermediate surfactants are the compounds (I) to (V) described above which neither fall under the definition of hydrophilic surfactants (I) to (V) nor under the definition of hydrophobic surfactants (I) to (V).

[0203] In a preferred embodiment, the surfactant system S1 comprises the one or more hydrophobic surfactants in a total amount of 45 wt.% to 100 wt.% and the one or more hydrophilic surfactants in a total amount of 0 wt.% to 55 wt.%, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S1.

[0204] In a more preferred embodiment, the surfactant system S1 comprises the one or more hydrophobic surfactants in a total amount of 50 wt.% to 100 wt.% and the one or more hydrophilic surfactants in a total amount of 0 wt.% to 50 wt.% of the at least one hydrophilic surfactant, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S1.

[0205] In an even more preferred embodiment, the surfactant system S1 comprises the one or more hydrophobic surfactants in a total amount of 55 wt.% to 100 wt.% and the one or more hydrophilic surfactants in a total amount of 0 wt.% to 45 wt.%, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S1.

[0206] In an embodiment, the surfactant system S2 comprises the one or more hydrophobic surfactants in a total amount of 0 wt.% to 45 wt.% and the one or more hydrophilic surfactants in a total amount of 55 wt.% to 100 wt.%, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S2.

[0207] In another embodiment, the surfactant system S2 comprises the one or more hydrophobic surfactants in a total amount of 0 wt.% to 35 wt.% and the one or more hydrophilic surfactants in a total amount of 65 wt.% to 100 wt.%, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S2.

[0208] In yet another embodiment, the surfactant system S2 comprises the one or more hydrophobic surfactants in a total amount of 0 wt.% to 25 wt.% and the one or more hydrophilic surfactants in a total amount of 75 wt.% to 100 wt.%, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S2.

[0209] Preferably however, surfactant system S2 does not comprise any hydrophobic surfactants (and thus comprises the one or more hydrophilic surfactants in a total amount of 100 wt.%, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S2).

[0210] The weight ratio of the overall amount of hydrophobic surfactant(s) (as comprised in surfactant system 1 and, if applicable, in surfactant system 2) to the overall amount of hydrophilic surfactant(s) (as comprised in surfactant system 2 and, if applicable, in surfactant system 1) is preferably in the range of 5:1 to 1:5, more preferably from 3:1 to 1:1.5, in particular from 3:1 to 1:1 and specifically from 2:1 to 1:1.

[0211] The surfactant systems S1 and S2 can be in solid, gel or liquid form.

[0212] In a specific embodiment,

- the hydrophobic surfactants are selected from compounds (I), (II), (III) and mixtures thereof, where
 - in compounds (I) R_1 is linear or branched C_8 - C_{16} -alkyl, preferably C_{10} - C_{16} -alkyl; $(x + z) \leq 5$, preferably 3 to 5, or x is 0, y_1 is 6 to 10, specifically 8, y_2 is 0, z is 3-8, specifically 4-7, R_3 is methyl and R_2 is hydrogen;
 - in compounds (II) R_4 is a linear or branched C_9 - C_{15} -alkyl; G^1 is selected from the group consisting of glucose, xylose and mixtures thereof; and m is preferably from 1.05 to 2.5, more preferably m from 1.10 to 1.8, in particular from 1.1 to 1.4;
 - in compounds (III) R_5 and R_6 are independently C_6 - C_{10} alkyl, where R_5 and R_6 have in sum at least 14, preferably at least 16 carbon atoms; and R_7 is an alkali metal cation;
- the hydrophilic surfactants are selected from compounds (I), (IV), (V) and mixtures thereof, where
 - in compounds (I) R_1 is linear or branched C_8 - C_{16} -alkyl, preferably C_{10} - C_{16} -alkyl; $(y_1 + y_2) = 0$ and $(x + z) > 6$, preferably ≥ 6.5 , more preferably 6.5 to 10, and R_2 is hydrogen;
 - in compounds (IV) R_8 is C_{10} - C_{14} alkyl; p is 0, $q = 2$ to 4; and M is an alkali metal cation;
 - in compounds (V) R_{10} is C_{10} - C_{14} alkyl and M is an alkali metal cation;
- the surfactant system S1 comprises the one or more hydrophobic surfactants in a total amount of 55 wt.% to 100 wt.%

and the one or more hydrophilic surfactants in a total amount of 0 wt% to 45 wt %, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S1;

- surfactant system S2 does not comprise any hydrophobic surfactants; and

- the weight ratio of the overall amount of hydrophobic surfactant(s) (as comprised in surfactant system 1 and, if applicable, in surfactant system 2) to the overall amount of hydrophilic surfactant(s) (as comprised in surfactant system 2 and, if applicable, in surfactant system 1) is in the range of 3:1 to 1:1.5, preferably from 3:1 to 1:1 and specifically from 2:1 to 1:1.

[0213] The liquid medium of the wash liquor preferably comprises water and more preferably is water. Water is generally tap water or any type of water customarily used for doing the laundry.

[0214] In an embodiment, the point in time T1 is the initiation of the wash cycle.

[0215] In an embodiment, the point in time T2 is in the range of 1 second to 15 minutes from the initiation of the wash cycle.

[0216] In another embodiment, the point in time T2 is in the range of 30 seconds to 10 minutes from the initiation of the wash cycle.

[0217] In another embodiment, the point in time T2 is in the range of 1 minute to 15 minutes from the initiation of the wash cycle.

[0218] In yet another embodiment, the point in time T2 is in the range of 2 minutes to 12 minutes from the initiation of the wash cycle.

[0219] In yet another embodiment, the point in time T2 is in the range of 3 minutes to 10 minutes from the initiation of the wash cycle.

[0220] In yet another embodiment, the point in time T2 is in the range of 4 minutes to 8 minutes from the initiation of the wash cycle.

[0221] In yet another embodiment, the point in time T2 is in the range of 5 minutes to 7 minutes from the initiation of the wash cycle.

[0222] Preferably, the point in time T2 is in the range of 2 minutes to 15 minutes, more preferably 2 minutes to 12 minutes, and specifically 2 minutes to 10 minutes from the initiation of the wash cycle.

[0223] In an embodiment, the point in time T3 is in the range of 30 seconds to 30 minutes from the initiation of the wash cycle (and after T2, of course).

[0224] In another embodiment, the point in time T3 is in the range of 1 minute to 25 minutes from the initiation of the wash cycle (and after T2, of course).

[0225] In another embodiment, the point in time T3 is in the range of 2 minutes to 20 minutes from the initiation of the wash cycle (and after T2, of course).

[0226] In yet another embodiment, the point in time T3 is in the range of 3 minutes to 20 minutes from the initiation of the wash cycle (and after T2, of course).

[0227] Preferably, the point in time T3 is in the range of 5 minutes to 20 minutes from the initiation of the wash cycle (and after T2, of course).

[0228] T4, T5, etc. are of course after the preceding point of time T3, T4 etc. The time interval (between T(x) and T(x-1)) is generally at least one 1 second, e.g. 1 second to 10 minutes or 1 minute to 5 minutes.

[0229] If the method of the invention is carried out with the above surfactant system S comprising both surfactant systems 1 and 2, where surfactant system S2 is in a delayed release form, the points in time after T1 (or beginning with T2) may be a continuum if the surfactants of surfactant system S2 are released continually and not in one swoop or portion-wise.

[0230] In an embodiment, the wash cycle in the washing machine is of at least 1 minute, preferably of at least 15 minutes. Generally, it is up to 4 hours, e.g. up to 3 or up to 2 hours.

[0231] In an embodiment, the surfactant systems S1 and S2 or the surfactant system S can be added manually or by means of an injector system or by means of a pump system at the pertinent points in time.

[0232] In an embodiment, the surfactant systems S1 and S2 can be added as individual pods which would release the respective surfactant systems at specific time interval, where the pods containing surfactant system S2 release this with a temporal delay as compared to the pods containing surfactant system S1.

[0233] In an embodiment, the portions can be added as pod in pod, capsule in capsule, pellets of various surfactants which release the specific surfactants or systems S1 and S2, respectively, at a specific time point.

[0234] In an embodiment, the method of laundering articles can be implemented in an automatic manner by computer implemented program of dosing the surfactant system.

[0235] In an embodiment, the wash liquor further comprises water.

[0236] The surfactant systems S1 and S2 may be used as such, i.e. as single surfactants or as mixtures of different

surfactants, but are more often used in the form of detergent systems which contain, in addition to the respective surfactant system S1 or S2, one or more additives. Also when a surfactant system S is used which contains both surfactant systems S1 and S2 (surfactant system S2 in a delayed release form), this may be used in the form of detergent systems which contain, in addition to the surfactant systems S1 and S2, one or more additives. The additives may however also be added separately from the surfactant systems to the wash liquor or the laundry. The composition and the kit according to the invention may as well contain one or more additives. Suitable additives are described in the following.

Additives

[0237] Suitable additives are those customarily used in laundry detergent compositions. Examples include, but are not limited to, chelating agents, enzymes, builders, bleaching agents, fragrances, fillers, anti-static agent, odor capturing agent, fiber protection agents, colour protection agents, soil releasing agents, UV protection agent, anti-pilling agent, viscosity control agents, stabilizers, optical brightener, soaps, silicon based defoamers, colourants, solvents and mixtures thereof.

Chelating agents

[0238] Examples for suitable chelating agents, also termed sequestering agents, are an amino carboxylic acid, a condensed phosphate, a phosphonate and a polyacrylate. In general, a chelating agent is a molecule capable of coordinating (i.e., binding) the metal ions commonly found in natural water to prevent the metal ions from interfering with the action of the other detergents ingredients of a composition. Useful aminocarboxylic acids include, for example, n-hydroxyethyliminodiacetic acid, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), N-hydroxyethyl ethylenediaminetriacetic acid (HEDTA), diethylenetriamine pentaacetic acid (DTPA), methylglycinediacetic acid (MGDA) and glutamic acid diacetic acid (GLDA). Examples of condensed phosphates are sodium and potassium orthophosphate, sodium and potassium pyrophosphate, sodium tripolyphosphate and sodium hexametaphosphate.

Enzymes

[0239] Enzymes can be used for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains and for the prevention of refugee dye transfer as well as for fabric restoration. Preferred enzymes are selected from cellulases, proteases, amylases, lipases, mannanases and mixtures thereof. The choice of the enzymes is governed by several factors such as the pH-activity and/or stability optima, the thermostability, the stability versus active detergents and the builders. Along with enzymes, enzyme stabilizing systems may also be used, such as for example, calcium ions, boric acid, boronic acids, propylene glycol and short chain carboxylic acids.

Builders

[0240] Detergent builders serve to assist in controlling mineral hardness. Inorganic or phosphorus-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanol ammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates.

[0241] Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio from 1.6:1 to 3.2:1 and the layered silicates.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates. Aluminosilicate builders are of great importance. Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally occurring aluminosilicates or synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X.

[0242] Organic detergent builders include a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form but can also be added in the form of a neutralized salt. When utilized in the salt form, alkali metals, such as sodium, potassium, lithium and alkanolammonium salts are preferred.

[0243] One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds.

[0244] Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxybenzene-2,4,6-trisulphonic acid and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine

tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5 tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof. Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of importance for liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Fatty acids, e.g., C₁₂ - C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity.

Bleaching Agents

[0245] The bleaching agents may be bleach catalysts or bleach activators and combinations thereof.

[0246] Bleach catalysts can be selected from the group of oxaziridinium-based bleach catalysts, bleach-boosting transition metal salts or transition metal complexes such as, for example, manganese-, iron-, cobalt-, ruthenium- or molybdenum-salen complexes or carbonyl complexes. Manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands and cobalt-, iron-, copper- and ruthenium-amine complexes.

[0247] Bleach activators are, for example, tetraacetyl ethylene diamine, tetraacetylmethylene diamine, tetraacetylglucuril, tetraacetylhexylenediamine, acylated phenolsulfonates such as for example n-nonanoyloxybenzene sulfonates or isononanoyloxybenzene sulfonates, N-methylmorpholinium acetonitrile salts ("MMA salts"), trimethylammonium acetonitrile salts, N-acylimides such as, for example, N-nonanoylsuccinimide, 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine ("DADHI") or nitrile quats (trimethylammonium acetonitrile salts).

Fragrances

[0248] Suitable fragrances are those derived from natural sources or are synthetic aromatic substances. Natural aromatic substances are, for example, extracts from blossom (lilies, lavender, roses, jasmine, neroli, ylang-ylang), from stems and leaves (geranium, patchouli, petitgrain), from fruit (aniseed, coriander, caraway, juniper), from fruit peel (bergamot, lemons, oranges), from roots (mace, angelica, celery, cardamom, costus, iris, calmus), from wood (pinewood, sandalwood, guaiacum wood, cedarwood, rose-wood), from herbs and grasses (tarragon, lemon grass, sage, thyme), from needles and twigs (spruce, pine, scots pine, mountain pine), from resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Typical synthetic aromatic substances are, for example, products of the ester, ether, aldehyde, ketone, alcohol or hydrocarbon type. Aromatic substance compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styrallyl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having from 8 to 18 hydrocarbon atoms, citral, citronellal, citronellyl oxyacetaldehyde, cyclamen aldehyde, hydroxy citronellal, linal and bourgeonal; the ketones include, for example, the ionones, isomethylionone and methyl cedryl ketone; the alcohols include, for example, anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenyl ethyl alcohol and terpinol; and the hydrocarbons include mainly the terpenes and balsams. Ethereal oils of relatively low volatility, which are chiefly used as aroma components, are also suitable for fragrance, e.g. sage oil, camomile oil, clove oil, melissa oil, oil of cinnamon leaves, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavandin oil.

Fillers

[0249] A typical filler does not perform as a cleaning agent per se, but cooperates with the cleaning agent to enhance the overall cleaning capacity of the composition. Examples of fillers are, but not limited to, sodium sulfate, sodium chloride, starch and sugars.

Anti-static agent

[0250] An anti-static agent can generate a static reduction when compared with fabric that is not subjected to treatment. It has been observed that fabric treated using the composition according to the invention exhibit more constant percent static reduction compared with commercially available liquid softeners.

[0251] Suitable anti-static agents are for example those commonly used in the laundry drying industry to provide anti-static properties. Exemplary anti-static agents include those quaternary compounds mentioned in the context of softening agents. Accordingly, a benefit of using conditioning agents including quaternary groups is that they may additionally provide anti-static properties.

Odor capturing agents

[0252] In general, odor capturing agents are believed to function by capturing or enclosing certain molecules that provide an odor. Exemplary odor capturing agents include cyclodextrins, and zinc ricinoleate.

Fiber protection agents

[0253] Fiber protection agents coat the fibers of fabrics to reduce or prevent disintegration and/or degradation of the fibers. Exemplary fiber protection agents include cellulosic polymers.

Colour protection agents

[0254] Colour protection agents serve for coating the fibers of the fabric to reduce the tendency of dyes to escape the fabric into water. Exemplary colour protection agents include quaternary ammonium compounds and surfactants. An exemplary quaternary ammonium colour protection agent includes di-(nortallow carboxyethyl) hydroxyethyl methyl ammonium methylsulfate that is available under the name Varisoft WE 21 CP from Evonik-Goldschmidt Corporation. An exemplary surfactant colour protection agent is available under the name Varisoft CCS-1 from Evonik-Goldschmidt Corporation. An exemplary cationic polymer colour protection agent is available under the name Tinofix CL from CIBA. Additional colour protection agents are available under the names colour Care Additive DFC 9, Thiotan TR, Nylofixan P-Liquid, Polymer VRN, Cartaretin F-4, and Cartaretin F-23 from Clariant; EXP 3973 Polymer from Alco; and Coltide from Croda.

Soil releasing agents

[0255] Soil releasing agents serve for coating the fibers of fabrics to reduce the tendency of soils to attach to the fibers. Exemplary soil releasing agents include polymers such as those available under the names Repel-O-Tex SRP6 and Repel-O-Tex PF594 from Rhodia; TexaCare 100 and TexaCare 240 from Clariant; and Sokalan HP22 from BASF.

Optical brighteners

[0256] Optical brightening agents impart fluorescing compounds to the fabric. In general, fluorescing compounds have a tendency to provide a bluish tint that can be perceived as imparting a brighter colour to fabric. Exemplary optical brighteners include stilbene derivatives, biphenyl derivatives, and coumarin derivatives. An exemplary biphenyl derivative is distyryl biphenyl disulfonic acid sodium salt. An exemplary stilbene derivative includes cyanuric chloride/diaminos-tilbene disulfonic acid sodium salt. An exemplary coumarin derivative includes diethylamino coumarin. Exemplary optical brighteners are available under the names Tinopal CBS-CL, Tinopal CBS-X, and Tinopal CBS SP Slurry from BASF. It should be noted, however, that an overall reduction in yellowing is observed when using the composition of the invention in elevated dryer temperatures without the addition of optical brightening agents.

UV protection agent

[0257] UV protection agents serve to provide the fabric with enhanced UV protection. In the case of clothing, it is believed that by applying UV protection agents to the clothing, it is possible to reduce the harmful effects of ultraviolet radiation on skin provided underneath the clothing. As clothing becomes lighter in weight, UV light has a greater tendency to penetrate the clothing and the skin underneath the clothing may become sunburned. An exemplary UV protection agent includes Tinosorb FD from BASF.

Anti-pilling agent

[0258] Anti-pilling agents act on portions of the fiber that stick out or away from the fiber. Anti-pilling agents can be available as enzymes such as cellulase enzymes. Exemplary cellulase enzyme anti-pilling agents are available under the names Laverly C Bright from BASF, Puradex from Genencor and Endolase and Carezyme from Novozyme.

Viscosity control agents

[0259] Viscosity control agents can be organic or inorganic in nature. Examples of organic viscosity modifiers are fatty acids and esters, fatty alcohols, and water-miscible solvents such as short chain alcohols. Examples of inorganic viscosity control agents are water-soluble ionizable salts. A wide variety of ionizable salts can be used. Examples of suitable salts

are the halides of the group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. Calcium chloride is preferred. The ionizable salts are particularly useful during the process of mixing the ingredients to make the liquid compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in such compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 6,000 parts per million (ppm), preferably from about 20 to about 4,000 ppm by weight of the composition.

Inorganic viscosity/dispersibility control agents

[0260] Inorganic viscosity/dispersibility control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition.

Stabilizers

[0261] Stabilizers such as hydrogen peroxide serve to stabilize preservatives such as Kathon CG/ICP for long term, shelf-life stability. Stabilizers may be included in the composition of the invention to control the degradation of preservatives and can range from about 0.05% up to about 0.1% by weight. Preservatives such as Kathon CG/ICP available from Rohm and Haas may be added to the composition of the invention from about 0.05 weight percent up to about 0.15 weight percent. Other preservatives that may be useful in the composition of the invention, which may or may not require use of stabilizers, include but are not limited to Ucaricide available from Dow, Neolone M-10 available from Rohm & Haas, and Korolone B 119 also available from Rohm & Haas.

Compositions

[0262] The present invention relates moreover to a composition comprising

- i) a surfactant system S comprising at least one hydrophobic surfactant and at least one hydrophilic surfactant, and
- ii) optionally additives,

wherein the at least one hydrophobic surfactant and at least one hydrophilic surfactant are preferably as defined above;

where at least 10% by weight of the hydrophilic surfactant, based on the total weight of the hydrophilic surfactant(s) present in the surfactant system S, is present in a delayed release form.

[0263] Preferably, at least 20% by weight, more preferably at least 50% by weight, in particular at least 80% by weight, and specifically 100% by weight of the hydrophilic surfactant(s), based on the total weight of the hydrophilic surfactant(s) present in the surfactant system S, is present in a delayed release form.

[0264] Delayed release forms are generally known to the skilled person. For instance, the composition can contain the hydrophobic surfactant(s) and the hydrophilic surfactant(s) in a physically separated form, where at least a part of the hydrophilic surfactant(s) is formulated thusly that its release into the liquid medium is delayed as compared to that of the hydrophobic surfactant(s). An example for such a surfactant system is the formulation of the hydrophobic surfactant(s) and at least a part of the hydrophilic surfactant(s) in separate, individual pods, where the walls of these pods are conceived thusly that the pod containing (at least a part of) the hydrophilic surfactant(s) releases its content into the liquid medium with a time lag after the pod containing the hydrophobic surfactant(s) has released its content. For example, the wall of the pod containing the hydrophobic surfactant(s) is thinner and/or better soluble or degradable in the liquid medium than the wall of the pod containing (at least a part of) the hydrophilic surfactant(s). Another example for such a surfactant system is a detergent pod wherein at least a part of the hydrophilic surfactant(s) is in a compartment within a pod containing the hydrophobic surfactant(s) (and the remainder of the hydrophilic surfactant(s), if applicable) (pod-in-pod system), where

the nature or thickness of the wall of said compartment containing (at least a part of) the hydrophilic surfactant(s) is thus that the latter is released from the compartment with a time delay as compared to the release of the hydrophobic surfactant(s). This can be obtained, for instance, by using a wall of the outer pod which is thinner and/or better soluble or degradable in the liquid medium into which the surfactants are to be released (generally water) and a denser and/or less soluble or degradable wall of the inner pod/compartment. Yet another example is a capsule in a capsule with an analogous function. In yet another example, if the hydrophobic and hydrophilic surfactants are solid, at least a part of the hydrophilic surfactant(s) is present as granules, pellets, pearls or similar forms coated with a coating which delays its/their dissolution in the liquid medium in which the surfactants are to be used (generally water). Suitable coating materials are known to those skilled in the art and include for example polymers with a lagging solubility in water, such as Pluronic® block copolymers. The hydrophobic surfactant(s) and the remainder of the hydrophilic surfactant(s), if any, are not coated and can be present in any solid form, as long as this dissolves in the liquid medium before the coated form of the hydrophilic surfactant(s); e.g. as a powder or also as granules, pellets, pearls and the like. In this case, the composition is simply a solid mixture of the hydrophobic and the hydrophilic surfactants, where at least a part of the hydrophilic surfactant(s) is present in a suitably coated form.

[0265] Alternatively, the present invention relates to a composition comprising

i) a surfactant system S comprising surfactant system S1 and surfactant system S2 as defined above, and

ii) optionally additives,

[0266] where at least 10% by weight of the surfactant system S2, based on the total weight of the surfactant system S2 present in the surfactant system S, is present in a delayed release form.

[0267] Preferably, at least 20% by weight, more preferably at least 50% by weight, in particular at least 80% by weight, and specifically 100% by weight of the surfactant system S2, based on the total weight of the surfactant system S2 present in the surfactant system S, is present in a delayed release form.

[0268] As explained above, delayed release forms are generally known. In this case, for instance, the composition can contain the surfactant systems S1 and S2 in a physically separated form, where at least a part of surfactant system S2 is formulated thusly that its release into the liquid medium is delayed as compared to that of surfactant system S1. An example for such a surfactant system is the formulation of surfactant system S1 and at least a part of surfactant system S2 in separate, individual pods, where the walls of these pods are conceived thusly that the pod containing (at least a part of) surfactant system S2 releases its content into the liquid medium with a time lag after the pod containing surfactant system S1 has released its content. For example, the wall of the pod containing surfactant system S1 is thinner and/or better soluble or degradable in the liquid medium than the wall of the pod containing (at least a part of) surfactant system S2. Another example for such a surfactant system is a detergent pod wherein at least a part of surfactant system S2 is in a compartment within a pod containing surfactant system S1 (and the remainder of surfactant system S2, if applicable) (pod-in-pod system), where the nature or thickness of the wall of said compartment containing (at least a part of) surfactant system S2 is thus that the latter is released from the compartment with a time delay as compared to the release of surfactant system S1. This can be obtained, for instance, by using a wall of the outer pod which is thinner and/or better soluble or degradable in the liquid medium into which the surfactants are to be released (generally water) and a denser and/or less soluble or degradable wall of the inner pod/compartment. Yet another example is a capsule in a capsule with an analogous function. In yet another example, if surfactant systems S1 and S2 are solid, at least a part of surfactant system S2 is present as granules, pellets, pearls or similar forms coated with a coating which delays its dissolution in the liquid medium in which the surfactants are to be used (generally water). Suitable coating materials are known to those skilled in the art and include for example polymers with a lagging solubility in water, such as Pluronic® block copolymers. Surfactant system S1 and the remainder of surfactant system S2, if any, are not coated and can be present in any solid form, as long as this dissolves in the liquid medium before the coated surfactant system S2 form; e.g. as a powder or also as granules, pellets, pearls and the like. In this case, the composition is simply a solid mixture of surfactant systems S1 and S2, where at least a part of surfactant S2 is present in a suitably coated form.

[0269] Suitable additives which are optionally present in the composition of the invention are those described above. They can be present in admixture with the hydrophobic surfactant(s), with the hydrophilic surfactant(s), with both or physically separated from both, e.g. in a separate pod within an outer pod, or as separate granules, pellets or pearls in the afore described solid mixture. If more than one additive is contained, the two or more additives can be separated physically from each other or can be used in admixture. Alternatively, the additives can be present in admixture with surfactant system S1, with surfactant system S2, with both or physically separated from both, e.g. in a separate pod within an outer pod, or as separate granules, pellets or pearls in the afore described solid mixture. If more than one additive is contained, the two or more additives can be separated physically from each other or can be used in admixture.

[0270] In an embodiment, the composition comprises the surfactant system S in an amount in the range of 5 wt% to 90 wt%, based on the total weight of the composition.

[0271] As can be understood from the above, the composition of the invention may be of any suitable form, for example powders or granules, liquids, gels or mixed form thereof. They may be prepared by methods well known to those skilled in the art.

[0272] If the composition of the invention is a liquid or a gel, it also contains water.

[0273] If the composition of the invention comprises one or more of the above additives and/or water, these are generally contained in amounts customary for laundry detergent compositions.

Use

[0274] The present invention is moreover directed to the use of the composition of the invention for laundering articles.

Kit of parts

[0275] The present invention is also directed to a kit of parts comprising at least two parts, where the first part comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant; and the second part comprises at least one hydrophilic surfactant, but no hydrophobic surfactant, where the hydrophobic and the hydrophilic surfactants are preferably as defined above, where the kit of parts is capable of being used in the method of the invention for laundering articles.

[0276] In an alternative embodiment, the present invention is also directed to a kit of parts comprising at least two parts, where the first part comprises surfactant system S1 and the second part comprises surfactant system S2, where surfactant systems S1 and S2 are as defined above.

[0277] While in the above-described compositions at least a part of surfactant system S2 is in a delayed release form to allow its release into the liquid system after surfactant system S1 has been released into it, in a kit of parts this is not necessary, and surfactant system S2 can be formulated in any form (as long as this makes technically sense for the specific surfactant(s) contained therein, of course). In a kit of parts, surfactants system S1 and at least a part of surfactant system S2 (or in case of the first alternative the at least one hydrophobic surfactant and at least a part of the at least one hydrophilic surfactant) are formulated separately, but provided in such a form that they nevertheless form a functional unity. They form thus a true combination through a purpose-directed application. The functional unity is expressed for example in the fact that the parts contain the surfactants in such amounts that when mixed, they result in the desired weight ratio. Another way to express functional unity may be a use instruction explaining the combined use of the two or more parts of the kit. Yet another way to express functional unity may be a physical connection. For instance, the different parts of the kit may be bond to each other via an adhesive tape or strap or any other type of tie, or may be assembled in a common container, such as a box, package, basket etc. or packed together in a plastic foil.

[0278] In a preferred embodiment, the kit of parts is a kit of two parts, where the first part comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant; and the second part comprises at least one hydrophilic surfactant, but no hydrophobic surfactant. One or both parts can additionally contain one or more of the above-mentioned additives.

[0279] In another preferred embodiment, the kit of parts is a kit of two parts, where the first part comprises surfactant system S1 and the second part comprises surfactant system S2. One or both parts can additionally contain one or more of the above-mentioned additives.

[0280] In another preferred embodiment, the kit of parts is a kit of three parts, where the first part comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant; the second part comprises a part of the at least one hydrophilic surfactant, but no hydrophobic surfactant and the third part comprises the remainder of the at least one hydrophilic surfactant, but no hydrophobic surfactant. One, two or all three parts can additionally contain one or more of the above-mentioned additives.

[0281] In another preferred embodiment, the kit of parts is a kit of three parts, where the first part comprises surfactant system S1, the second part comprises a part of surfactant system S2 and the third part comprises the remainder of surfactant system S2. One or both parts can additionally contain one or more of the above-mentioned additives.

Advantages:

[0282] Significant improvement of the washing performance is observed with the method of laundering articles involving dosing of hydrophobic and hydrophilic surfactants of the present invention.

Embodiments

[0283] The present invention is illustrated in more detail by the following embodiments and combinations of embodiments which result from the corresponding dependency references and links:

1. A method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) at point in time T2 (which is after T1) supplying the wash liquor of step b), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally at least one hydrophobic surfactant, and resuming the wash cycle, and

d) if desired repeating step c) one or more times.

The method may also encompass following steps:

e) rinsing the laundering articles of the wash liquor, and

f) drying the laundered articles.

2. A method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) at point in time T2 (that is after T1) supplying the wash liquor of step b), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle, and

d) at point in time T3 and supplying the wash liquor of step c), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle.

The method may also encompass following steps:

e) rinsing the laundering articles of the wash liquor, and

f) drying the laundered articles.

3. A method of laundering articles, the method comprising the steps of:

a) providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant,

b) applying said wash liquor to the laundering articles and initiating a wash cycle at a point in time T1,

c) at point in time T2 (that is after T1) supplying the wash liquor of step b), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle,

d) at point in time T3 (that is after T2) supplying the wash liquor of step c) optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle,

d') at a point in time T4 (that is after T3) supplying the wash liquor of step d), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle;

d'') optionally: at a point in time T5 (that is after T4), supplying the wash liquor of step d'), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally also at least one hydrophobic surfactant, and resuming the wash cycle,, and

d''') is desired repeating step d'') (if this is carried out) one or more times (at a point in time T6, T7 etc.).

The method may also encompass following steps:

- e) rinsing the laundering articles of the wash liquor, and
f) drying the laundered articles.

4. The method according to embodiment 1 to 3, wherein the at least one hydrophobic surfactant and at least one hydrophilic surfactant is selected from

- a) at least one compound of formula (I),

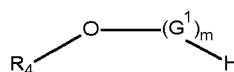


wherein

- R_1 is selected from linear or branched C_1 - C_{22} alkyl,
 R_2 is selected from H and linear or branched C_1 - C_{22} alkyl,
 A is CH_2-CH_2-O ,
 B is $CH_2-CH(R_3)-O$, wherein R_3 is linear or branched C_1 - C_{10} alkyl,
 x is an integer in the range from 0 to 35,
 $y1$ is an integer in the range from 0 to 60,
 $y2$ is an integer in the range from 0 to 35,
 z is an integer in the range from 0 to 35, and

wherein the sum of $x+y1+z+y2$ is at least 2;

- b) at least one compound of formula (II),

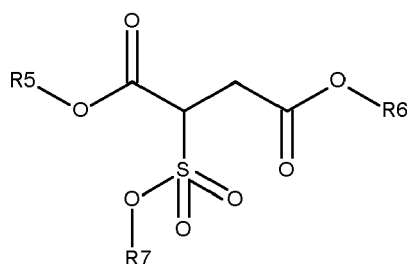


Compound of formula (II),

wherein

- R_4 is a linear or branched C_6 to C_{30} alkyl,
 G^1 is a monosaccharide residue having 5 or 6 carbon atoms,
 m is on average in the range of 1 to 10;

- c) at least one compound of formula (III),



Compound of formula (III),

wherein, each of R_5 and R_6 is a linear or branched C_4 - C_{22} alkyl, or a linear or branched unsaturated aliphatic C_4 - C_{22} hydrocarbonyl radical, and R_7 is a hydrogen atom or alkali metal or an alkaline earth metal cation equivalent,

- d) at least one compound of formula (IV)



wherein

R_8 is a linear or branched C_6 - C_{22} alkyl,
 D denotes CH_2-CHR_9-O , wherein R_9 is linear or branched C_1 - C_{10} alkyl, preferably methyl,
 E denotes CH_2-CH_2-O- ,
 p is an integer in the range from 0 to 10,
 q is an integer in the range from 0 to 5,
 M is H or an alkali metal or ammonium cation, or

e) at least one surfactant (V) which is selected from the group consisting of C_5 - C_{20} alkylbenzene sulfonic acids and salts thereof.

5. The method according to embodiment 4, where in the compound of formula (I), R_1 is linear or branched C_{10} - C_{16} alkyl, x = is 2 to 8, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

6. The method according to embodiment 5, wherein R_1 is branched C_{13} alkyl, x = is 2-4, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

7. The method according to embodiment 4, where in the compound of formula (I), R_1 is linear or branched C_{10} - C_{16} alkyl, x = is 4 to 10, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

8. The method according to embodiment 7, wherein R_1 is branched C_{13} - C_{15} alkyl, x = is 4 to 8, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

9. The method according to embodiment 4, where in the compound of formula (I), R_1 is linear or branched C_{10} - C_{16} alkyl, x = is 2 to 8, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

10. The method according to embodiment 9, wherein R_1 is branched C_{13} - C_{15} alkyl, x = is 2 to 6, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

11. The method according to embodiment 4, where in the compound of formula (I), R_1 is linear or branched C_{10} - C_{16} alkyl, x = is 4 to 10, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

12. The method according to embodiment 11, wherein R_1 is branched C_{13} - C_{15} alkyl, x = is 4 to 7, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

13. The method according to embodiment 4, the compound of formula (I), wherein R_1 is branched C_{10} - C_{16} alkyl, x = is 2-8, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

14. The method according to embodiment 13, wherein R_1 is branched C_{13} - C_{15} alkyl, x = is 2-8, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

15. The method according to embodiment 4, where in the compound of formula (I), R_1 is linear C_{12} - C_{14} alkyl, x = is 4-7, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

16. The method according to embodiment 15, wherein R_1 is linear C_{12} - C_{14} alkyl, x = is 7, $y_1 = 0$, $z = 0$, $y_2 = 0$, and R_2 is H.

17. The method according to embodiment 4, where in the compound of formula (I), R_1 is branched C_8 - C_{14} alkyl, x = is 0, $y_1 = 6-10$, $z = 6-10$, $y_2 = 0$, and R_2 is H.

18. The method according to embodiment 17, wherein R_1 is branched C_{10} alkyl, x = is 0, $y_1 = 8$, $z = 7$, $y_2 = 0$, and R_2 is H, and where preferably is R_3 methyl.

19. The method according to embodiment 4, where in the compound of formula (I), R_1 is branched, unsubstituted C_8 - C_{14} alkyl, x = is 0, $y_1 = 6-10$, $z = 2-6$, $y_2 = 0$, and R_2 is H, and where preferably is R_3 methyl.

20. The method according to embodiment 19, wherein R_1 is branched C_{10} alkyl, x = is 0, $y_1 = 8$, $z = 4$, $y_2 = 0$, and R_2 is H, and where preferably is R_3 methyl.

21. The method according to any of preceding embodiments 4 to 20, where R_1O is derived from a linear or branched C_4 to C_{18} alkanol.

22. The method according to embodiment 21, where R_1O is derived from a C_8 to C_{18} alkanol.

23. The method according to embodiment 22, where R_1O is derived an alcohol selected from the group consisting of 2-propylheptanol, lauryl alcohol, linear or branched tridecyl alcohol, myristyl alcohol, C_{13} - C_{15} oxo alcohols and mixtures thereof.

24. The method according to embodiment 4, where in the compound of formula (II), R_4 is a linear or branched C_6 to C_{20} alkyl.

25. The method according to embodiment 24, where in the compound of formula (II), R_4 is a linear or branched C_8 to C_{15} alkyl.

26. The method according to any of embodiments 4, 24 or 25, where the compound of formula (II), G^1 is selected from the group consisting of the group consisting of ribulose, xylulose, ribose, arabinose, xylose, lyxose, galactose, mannose, rhamnose, glucose and mixtures thereof.

27. The method according to embodiment 26, where G^1 is selected from the group consisting of glucose, xylose,

arabinose, rhamnose and mixtures thereof.

28. The method according to embodiment 27, where G^1 is selected from the group consisting of glucose, xylose and mixtures thereof.

29. The method according to any of embodiments 4 and 24 to 28, where m is from 1.05 to 2.5.

30. The method according to embodiment 29, where m is from 1.10 to 1.8.

31. The method according to embodiment 30, where m is from 1.1 to 1.4.

32. The method according to any of embodiments 4 and 24 to 31, where in the compound of formula (II), R_4 is a branched C_9 or C_{10} or C_{13} alkyl and m is in the range of 1.1 to 1.8.

33. The method according to embodiment 32, wherein m is 1.3.

34. The method according to embodiment 4, where in the compound of formula (III), each of R_5 and R_6 is a linear or branched C_{10} - C_{20} alkyl or a linear or branched unsaturated aliphatic C_{10} - C_{20} hydrocarbyl radical, and R_7 is a hydrogen atom or alkali metal or an alkaline earth metal cation equivalent.

35. The method according to embodiment 4, where in the compound of formula (III), each of R_5 and R_6 is a linear or branched C_6 - C_{20} alkyl or a linear or branched unsaturated aliphatic C_6 - C_{20} hydrocarbon radical, and R_7 is a hydrogen atom or alkali metal or an alkaline earth metal cation equivalent.

36. The method according to embodiment 35, wherein each of R_5 and R_6 is a linear or branched C_6 - C_{12} alkyl or a linear or branched unsaturated aliphatic C_6 - C_{12} hydrocarbon radical, preferably a C_6 - C_{12} alkyl; and R_7 is an alkali metal or an alkaline earth metal cation equivalent.

37. The method according to embodiment 35, wherein each of R_5 and R_6 is a linear or branched C_8 alkyl or a linear or branched unsaturated aliphatic C_8 hydrocarbon radical, and R_7 is a hydrogen atom or alkali metal or an alkaline earth metal cation equivalent.

38. The method according to embodiment 4, where in the compound of formula (IV), R_8 is linear or branched C_{10} - C_{16} alkyl, preferably C_{10} - C_{14} alkyl; p is 0 to 8, q is 0 to 6, M = alkali metal, and wherein the sum of $p+q$ is at least 2.

39. The method according to embodiment 38, wherein R_8 is linear or branched C_{12} alkyl, p is 0, q is 3, M = sodium, and wherein the sum of $p+q$ is at least 2.

40. The method according to embodiment 4, where the surfactant (V) is a C_5 - C_{20} alkylbenzene sulfonic acid or a salt thereof.

41. The method according to embodiment 40, where the surfactant (V) is a C_5 - C_{15} alkylbenzene sulfonic acid or a salt thereof.

42. The method according to embodiment 40, where the surfactant (V) is a C_8 - C_{16} alkylbenzene sulfonic acid or a salt thereof.

43. The method according to embodiment 42, where the surfactant (V) is the alkali metal salt of a C_8 - C_{16} alkylbenzene sulfonic acid.

44. The method according to embodiment 43, where the surfactant (V) is the alkali metal salt of a C_{10} - C_{14} alkylbenzene sulfonic acid.

45. The method according to any one of the embodiments 4 to 44 wherein the hydrophobic surfactant is selected from the group consisting of

a) at least one compound of formula (I), wherein

- $(y_1 + y_2) = 0$ and $(x + z) \leq 5$, preferably 3 to 5; or
- $(x + z) = 0$; or
- $(y_1 + y_2) \neq 0$, $(x + z) \neq 0$ and $(x+z) - (y_1 + y_2) \leq 2$; preferably ≤ 0 ; or
- R_2 is linear or branched C_1 - C_{22} alkyl;

where the last condition can apply simultaneously with one or more of the first three conditions;

b) at least one compound of formula (II); and

c) at least one compound of formula (III), wherein R_5 and R_6 have together at least 14 carbon atoms;

and wherein

the hydrophilic surfactant is selected from the group consisting of

a) at least one compound of formula (I), wherein

- $(y_1 + y_2) < 3$ and $(x + z) \geq 6$, preferably ≥ 6.5 , e.g. 6.5 to 10 or 7 to 10; and R_2 is hydrogen

c) at least one compound of formula (III), wherein R_5 and R_6 have together at most 12 carbon atoms; wherein

preferably R_7 is an alkali metal or an alkaline earth metal cation (equivalent);

d) at least one compound of formula (IV), wherein M is preferably an alkali metal or ammonium cation; and

e) at least one compound of formula (V), which is preferably a salt of a C_5 - C_{20} alkylbenzene sulfonic acid.

46. The method according to embodiment 45, where, irrespective of whether the compound (I) is a hydrophobic or a hydrophilic surfactant, R_1 is linear or branched C_8 - C_{16} alkyl, preferably linear or branched C_{10} - C_{16} alkyl; R_2 is H and R_3 is methyl.

47. The method according to any of embodiments 45 or 46, where in hydrophobic compounds (I), $(y_1 + y_2) = 0$ and $(x + z) \leq 5$, preferably 3 to 5; or $x + z = 3-8$, specifically 4-7, $y_1 + y_2 = 6$ to 10, specifically 8; where preferably $(y_1 + y_2) = 0$ and $(x + z) = 3$ to 5; or x is 0, y_1 is 6 to 10, specifically 8, y_2 is 0, and z is 3-8, specifically 4-7.

48. The method according to embodiment 45, where in hydrophobic compounds (II), R_4 is a linear or branched C_9 - C_{15} -alkyl; G^1 is selected from the group consisting of glucose, xylose and mixtures thereof; and m is preferably from 1.05 to 2.5, more preferably m from 1.10 to 1.8, in particular from 1.1 to 1.4.

49. The method according to embodiment 45, where in hydrophobic compounds (III) R_5 and R_6 are independently C_6 - C_{10} alkyl, where R_5 and R_6 have in sum at least 14, preferably at least 16 carbon atoms; and R_7 is an alkali metal cation.

50. The method according to embodiment 45, where in hydrophilic compounds (IV) R_8 is C_{10} - C_{14} alkyl; p = is 0, q = 2 to 4; and M is an alkali metal cation.

51. The method according to embodiment 45, where in hydrophilic compounds (V) R_{10} is C_{10} - C_{14} alkyl and M is an alkali metal cation.

52. The method according to any one of the embodiments 1 to 51, wherein the surfactant system S1 comprises 45 wt.% to 100 wt.% of hydrophobic surfactant and 0 wt.% to 55 wt.% of hydrophilic surfactant, based on the surfactant system S1.

53. The method according to any one of the embodiments 1 to 52, wherein the surfactant system S1 comprises 50 wt.% to 100 wt.% of hydrophobic surfactant and 0 wt.% to 50 wt.% of hydrophilic surfactant, based on the surfactant system S1.

54. The method according to any one of the embodiments 1 to 53, wherein the surfactant system S1 comprises 55 wt.% to 100 wt.% of hydrophobic surfactant and 0 wt.% to 45 wt.% of hydrophilic surfactant, based on the surfactant system S1.

55. The method according to any one of the embodiments 1 to 54, wherein the surfactant system S2 comprises 0 wt.% to 45 wt.% of hydrophobic surfactant and 55 wt.% to 100 wt.% of hydrophilic surfactant, based on the surfactant system S2.

56. The method according to any one of the embodiments 1 to 55, wherein the surfactant system S2 comprises 0 wt.% to 35 wt.% of hydrophobic surfactant and 65 wt.% to 100 wt.% of hydrophilic surfactant, based on the surfactant system S2.

57. The method according to any one of the embodiments 1 to 56, wherein the surfactant system S2 comprises 0 wt.% to 25 wt.% of hydrophobic surfactant and 75 wt.% to 100 wt.% of hydrophilic surfactant, based on the surfactant system S2.

58. The method according to any one of the embodiments 1 to 57, wherein the surfactant system S2 comprises 0 wt.% of hydrophobic surfactant and 100 wt.% of hydrophilic surfactant, based on the surfactant system S2.

59. The method according to embodiment 1 to 58, wherein point in time T1, is the initiation of the wash cycle.

60. The method according to embodiment 1 to 59, wherein point in time T2, is in the range of 1 second to 15 minutes from the initiation of the wash cycle.

61. The method according to embodiment 1 to 60, wherein point in time T2, is in the range of 30 second to 10 minutes from the initiation of the wash cycle.

62. The method according to embodiment 1 to 61, wherein point in time T2, is in the range of 1 minutes to 15 minutes from the initiation of the wash cycle.

63. The method according to embodiment 1 to 62, wherein point in time T2, is in the range of 2 minutes to 12 minutes from the initiation of the wash cycle.

64. The method according to embodiment 1 to 63, wherein point in time T2, is in the range of 3 minutes to 10 minutes from the initiation of the wash cycle.

65. The method according to embodiment 1 to 64, wherein point in time T2, is in the range of 4 minutes to 8 minutes from the initiation of the wash cycle.

66. The method according to embodiment 1 to 65, wherein point in time T2, is in the range of 5 minutes to 7 minutes from the initiation of the wash cycle.

67. The method according to embodiment 1 to 65, wherein the point in time T2 is in the range of 2 minutes to 15 minutes, preferably 2 minutes to 12 minutes, and specifically 2 minutes to 10 minutes from the initiation of the wash cycle.

68. The method according to any one of the embodiments 1 to 67, wherein the wash liquor further comprises water.

69. A composition comprising,

i) a surfactant system S comprising a mixture of at least one hydrophobic surfactant and at least one hydrophilic surfactant, and

ii) optionally additives,

wherein the at least one hydrophobic surfactant and at least one hydrophilic surfactant are as defined in any of embodiments 4 to 51;

where at least 10% by weight of the hydrophilic surfactant, based on the total weight of the hydrophilic surfactant(s) present in the surfactant system S, is present in a delayed release form.

70. The composition according to embodiment 69, wherein the amount of surfactant system S is in the range of 5 wt% to 90 wt%, based on the total weight of the composition

71. The composition according to any of embodiments 69 and 70, wherein the additives are selected from the group consisting of chelating agents, enzymes, builders, bleaching agents, fragrances, fillers, anti-static agent, odor capturing agent, fiber protection agents, colour protection agents, soil releasing agents, UV protection agent, anti-pilling agent, viscosity control agents, stabilizers, optical brightener, soaps, silicon based defoamers, colourants, solvents and mixtures thereof.

72. Use of the composition according to any of the embodiments 69 to 71 for laundering articles.

73. A kit of parts comprising at least two parts, where the first part comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant; and the second part comprises at least one hydrophilic surfactant, but no hydrophobic surfactant, where the hydrophobic and the hydrophilic surfactants are preferably as defined in embodiments 4 to 51; or where the first part comprises surfactant system S1 and the second part comprises surfactant system S2, where surfactant systems S1 and S2 are as defined in any of embodiments 1 to 58, where the kit of parts is capable of being used in a method for laundering articles according to any of the embodiments 1 to 68.

74. The kit of parts according to embodiment 73, where the first part comprises at least one hydrophobic surfactant, optionally at least one hydrophilic surfactant; and additives, where the additives are preferably as defined in embodiment 71, and the second part comprises at least one hydrophilic surfactant and optionally one or more additives, where the additives are preferably as defined in embodiment 71; or where the first part comprises surfactant system S1 and optionally additives, where the additives are preferably as defined in embodiment 71, and the second part comprises surfactant system S2 and optionally additives, where the additives are preferably as defined in embodiment 71.

Examples

[0284] The following examples are set forth below to illustrate the methods and results according to the disclosed subject matter. These examples are not intended to be inclusive of all aspects of the subject matter disclosed herein, but rather to illustrate representative methods, compositions, and results. These examples are not intended to exclude equivalents and variations of the present invention, which are apparent to one skilled in the art.

[0285] The surfactant systems were prepared as per following Table 1.

Surfactant (Ia): hydrophobic surfactant of formula (I); Lutensol® AO 3 from BASF, C₁₃-C₁₅ oxo alcohol ethoxylated with 3 EO on average.

Surfactant (Ib): hydrophobic surfactant of formula (I); Lutensol® TO 5 from BASF; iso-C₁₃-alcohol ethoxylated with 5 EO on average.

Surfactant (Ic): hydrophobic surfactant of formula (I); Lutensol® TDA 3 from BASF; branched C₁₃-alcohol ethoxylated with 3 EO on average.

Surfactant (Id): hydrophilic surfactant of formula (I); Lutensol® A 65 N from BASF; lauryl/myristyl alcohol ethoxylated with 7 EO on average.

Surfactant (Ie): hydrophobic surfactant of formula (I); Plurafac® LF 902 from BASF; alkoxylated fatty alcohol containing units derived from EO and higher alkylene oxides.

Surfactant (If): hydrophobic surfactant of formula (I); Plurafac® LF 903 from BASF; alkoxylated fatty alcohol containing units derived from EO and higher alkylene oxides.

Surfactant (Ig): hydrophilic surfactant of formula (I); Lutensol® LA 60 from BASF; lauryl/myristyl alcohol ethoxylated

with 7 EO on average.

Surfactant (Ih): hydrophobic surfactant of formula (I); Lutensol® TO 3 from BASF; iso-C₁₃-alcohol ethoxylated with 3 EO on average.

Surfactant (IIa): hydrophobic surfactant of formula (II); Glucopon® 800 from BASF; a glucose-containing ether.

Surfactant (IIIa): hydrophobic surfactant of formula (III); Lutensit® A-BO from BASF; sodium dioctylsulfosuccinate (60% in water/neopentyl glycol).

Surfactant (IVa): hydrophilic surfactant of formula (IV); Sensapol® ES-3K from Kensing; sodium lauryl ether sulfate + 3EO.

Surfactant (Va): hydrophilic surfactant of formula (V); BIO-SOFT® D-40 from Stepan; sodium salt of a C₁₂-alkylbenzene sulfonic acid.

[0286] Table 1 lists the surfactant systems as they would result if all respectively compiled surfactants were used in admixture (i.e. corresponding to a mixture of the surfactants in surfactant systems S1 and S2). These surfactant systems 1 to 5 are also used as comparative examples in the following experiments.

Table 1: Surfactant systems consisting of hydrophobic and hydrophilic surfactant and their weight proportions

Surfactant system 1 (SS1)		Surfactant system 2 (SS2)		Surfactant system 3 (SS3)		Surfactant system 4 (SS4)		Surfactant system 5 (SS5)	
Surfactant	wt%	Surfactant	wt%	Surfactant	wt%	Surfactant	wt%	Surfactant	wt%
IIa	27%	Ie	38%	If	38%	Ie	38%	Ie	38%
Ia	27%	Ib	12%	Ic	24%	Ib	12%	Ib	12%
Va*	46%	IVa*	50%	Id*	38%	Va*	50%	Id*	50%
*Hydrophilic surfactant									

[0287] The HLD of the single surfactants was calculated as follows:

$$\text{HLD} = -0.16 \text{ (or } -0.06^*) \times 16 - c_T(T-25) + \sigma$$

* in case of (Ie) and (If)

c_T of (Ia) to (Ih): -0.06

c_T of (IIa): 0

c_T of (IIIa), (IVa) and (Va): 0.01

[0288] σ values are either known from <https://www.stevenabbott.co.uk/practical-surfactants/cc.php> (e.g. (IIIa): σ = 2.55; (Va): σ = -0.9) or were determined according to the method described in <https://www.stevenabbott.co.uk/practical-surfactants/measure-cc.php>.

[0289] The HLD of the initial and of the final surfactant system was calculated from the HLD of the single surfactants contained in the initial and in the final surfactant system, respectively, by forming the sum of the individual HLD values in each case multiplied with the respective molar fraction x_i.

Conditions and evaluation:

[0290]

Stain set: Decane, tetradecane, hexadecane, and olive oil, all dyed with Oil Red O dye and filtered to remove excess solid dye.

Substrate: spun polyester napkins, stripped with high temperature (>80 °C) and high alkalinity (0.3%) to remove stain resistant coating, cut into 2.5" x 4" swatches

Staining protocol: 70 μL of dyed oil was pipetted onto the swatch and aged; alkane stains were aged for 24 h at room

temperature, and triglyceride stains were aged for 1 h at 50 °C.

Detergency evaluation: The primary detergency performance is determined by measuring the L*, a*, and b* values of the stained swatches before and after washing using a Mach5+ Colour Consult multispectral colour measurement instrument. A ΔE value is then calculated from the pre- and post-wash values. Higher ΔE values indicate better cleaning performance. If the difference in ΔE (with respect to control) is 1 or somewhat higher, the difference in colour is visually perceivable by the average human eye upon close observation. If the difference in ΔE (with respect to control) is ≥ 2 , the difference in colour is effortlessly perceivable by the average human eye.

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2}$$

L* - lightness with 0 being a perfect black of 0% reflectance or transmission; 50 a middle gray; 100 a perfect white of 100% reflectance or a perfect clear of 100% transmission

a* - redness-greenness of colour. Positive values of a* are red; negative values of a* are green; 0 is neutral

b* - yellowness-blueness of the colour. Positive values of b* are yellow, negative values of b* are blue, 0 is neutral.

Delta L* - lightness difference between sample and standard colours.

Delta a* - redness or greenness difference between sample and standard colours.

Delta b* - blueness-yellowness between sample and standard colours.

Example group A - Small scale experiments

[0291] These experiments were carried out in a Terg-O-Tometer. 2 swatches of each stain were used in each laundry experiment, for a total of 8 swatches and 560 μ L of oil. At the start of the wash cycle, the indicated surfactant system with the withheld hydrophilic surfactant (HS; as per table 2) was added to the wash liquor, the standardized stains and the ballast fabric were added, and the wash cycle was started. After a point in time T2 (as per tables 2a and 2b), the wash cycle was paused and the indicated portion of the withheld hydrophilic surfactant was dosed into the wash liquor. The wash cycle was resumed. The wash cycle was carried out at 60 rpm for 20 minutes with a total of 750 ppm surfactant (various temperatures, as indicated), and the rinse cycle was carried out at 60 rpm for 10 minutes. The swatches were then spun in an extractor to remove excess water, and then dried in a home-style dryer until fully dry.

Table 2a: Washing performance of surfactant system with dosing at time intervals

No.	SSx	Surfactants // initial amounts [ppm]	HS // added amount [ppm]	T2 [min]	Initial HLD	Final HLD	ΔE (Sum of Stains)	ΔE Difference
1	Comp-SS1	Ila / Ia / Va // 202.5/202.5/345	-	-	-2.55	-2.55	24.49	0
2	SS1	Ila / Ia / Va // 202.5/202.5/173	Va // 172	5	-1.79	-2.55	25.82	1.33
3		Ila / Ia / Va // 202.5/202.5/173	Va // 172	10	-1.79	-2.55	26.74	2.25
4		Ila / Ia / Va // 202.5/202.5/87	Va // 258	5	-1.14	-2.55	28.73	4.24
5		Ila / Ia / Va // 202.5/202.5/0	Va // 345	5	+0.10	-2.55	29.86	5.36
6	Comp-SS2	Ie / Ib / IVa // 281.25/93.75/375	-	-	-3.51	-3.51	46.23	0

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(continued)

No.	SSx	Surfactants // initial amounts [ppm]	HS // added amount [ppm]	T2 [min]	Initial HLD	Final HLD	ΔE (Sum of Stains)	ΔE Difference
7	SS2	Ie / Ib / IVa // 281.25/93.75/281.3	IVa // 93.75	10	-3.30	-3.51	49.02	2.79
8		Ie / Ib / IVa // 281.25/93.75/187.5	IVa // 187.5	2.5	-2.94	-3.51	50.13	3.89
9		Ie / Ib / IVa // 281.25/93.75/93.8	IVa1 281.25	2.5	-2.30	-3.51	47.42	1.18
- 10		Ie / Ib / IVa // 281.25/93.75/0	IVa // 375	2.5	-0.67	-3.51	51.16	4.93
11		Ie / Ib / IVa // 281.25/93.75/0	IVa // 375	5	-0.67	-3.51	50.02	3.78
12		Ie / Ib / IVa // 281.25/93.75/0	IVa // 375	7.5	-0.67	-3.51	50.68	4.45
13	Comp-SS3	If / Ic / Id // 281.25/187.5/281.25	-	-	-0.59	-0.59	31.73	0
14	SS3	If / Ic / Id // 281.25/187.5/210.9	Id // 70.3	2.5	-0.28	-0.59	35.03	3.30
15		If / Ic / Id // 281.25/187.5/140.6	Id // 140.6	2.5	+0.13	-0.59	33.08	1.35
- 16		If / Ic / Id // 281.25/187.5/140.6	Id // 140.6	10	+0.13	-0.59	33.57	1.84
17		If / Ic / Id // 281.25/187.5/0	Id // 281.25	2.5	+1.35	-0.59	34.28	2.55
18	Comp-SS4	Ie / Ib / Va // 281.25/93.75/375	-	-	-3.81	-3.81	45.25	0
19	SS4	Ie / Ib / Va // 281.25/93.75/0	Va // 375	2.5	-0.67	-3.81	47.47	2.22
- 20		Ie / Ib / Va // 281.25/93.75/0	Va // 375	5	-0.67	-3.81	47.25	2.00
21	Comp-SS5	Ie / Ib / Id // 281.25/93.75/375	-	-	-2.14	-2.14	47.79	0
22	SS5	Ie / Ib / Id // 281.25/93.75/0	Id // 375	2.5	-0.67	-2.14	53.41	5.62
23		Ie / Ib / Id // 281.25/93.75/0	Id // 375	5	-0.67	-2.14	53.64	5.85
HS hydrophilic surfactant T2 time of addition of withheld HS (min after start of the wash cycle)								

[0292] In the above experiments no. 1 to 23, washing and rinsing was carried out at 57°C.

[0293] In another group of experiments no. 24 to 28, using surfactant system SS3, washing and rinsing was carried out at 35°C. The conditions and results are compiled in table 2b.

Table 2b: Washing performance of surfactant system with dosing at time intervals

No.	SSx	Surfactants // initial amounts [ppm]	HS // added amount [ppm]	T2 [min]	Initial HLD	Final HLD	ΔE (Sum of Stains)	ΔE Difference
24	Comp-SS3	If / Ic / Id // 281.25/187.5/281.25	-	-	-1.93	-1.93	38.45	0
25	SS3	If / Ic / Id // 281.25/187.5/140.6	Id // 140.6	2.5	-1.20	-1.93	40.83	2.38
26		If / Ic / Id // 281.25/187.5/70.3	Id // 210.9	2.5	-0.65	-1.93	41.44	2.99
27		If / Ic / Id // 281.25/187.5/0	Id // 281.25	2.5	+0.03	-1.93	41.24	2.79
28		If / Ic / Id // 281.25/187.5/0	Id // 281.25	5	+0.03	-1.93	40.20	1.75

[0294] The above results show that adding a part or all of the hydrophilic surfactant some time after starting the wash cycle (and thus moving to more negative HLD values in the wash liquor in the course of the washing process; in the above experiments from as high as +1.35 to as low as -3.81 ; the final HLD being at least 0.2 lower than the initial HLD) leads to improved stain removal as compared to adding the complete amount of hydrophilic surfactant from the start. Even better results are obtained if the HLD profile in laundry was to start slightly positive to slightly negative and shift more negative throughout the laundry process (from $ca -1 \leq HLD \leq +0.2$ at the beginning of the wash cycle to $ca. -4 \leq HLD \leq -2$ at the end of the wash cycle (before rinsing)). The experiments described here use the surfactants themselves to control the HLD profile of the wash cycle.

[0295] The present data indicates that withholding some or all of the surfactant with the most negative σ value (most hydrophilic) for a certain time, and then shifting to more negative HLD by adding the withheld hydrophilic surfactant showed improvement in the detergency when compared to letting the whole surfactant system work from the start.

[0296] The results obtained for the surfactant system S1 were further evaluated for a composition having surfactant system and additives. The washing performance was evaluated for detergent formulations having surfactant system against swatches with oily stains, enzymatic stains and oxidizable stains.

Example group B - washing performance of compositions - full scale experiments

Conditions:

[0297]

Test equipment: Top Load Washing Machine, Model: WTW4800XQ4 from Whirlpool, Benton Harbor, Michigan, USA

Washing liquor: 64 L

Detergent dosage: 1.2 g/L

Washing time / temperature: 16 min at 30°C

Rinsing time / temperature: 5 min at 15°C

Fabric/liquor ratio: 42.1 g/L

Stains: assorted (oily, enzymatic, oxidizable); each 5.08 x 5.08 cm²

Stained fabric: polycotton, cotton, polyester (the latter only oily stains)

Ballast fabric: 100% cotton hand towels (8 pieces), 50/50 polyester/cotton AATCC dummy washload ballast by Testfabrics (10 pieces)

[0298] Method: A mixture of standardized stains sewn onto fabric were washed together amongst 2.70 kg of unsoiled, ballast fabric at 30 °C with the surfactant system described below. At the start of the wash cycle, the indicated surfactant system with the withheld hydrophilic surfactant (*; as per table 3; in the comparative examples no withheld surfactant; full dose) was added to the wash liquor, the standardized stains and the ballast fabric were added, and the wash cycle was started. After a point in time T2 (as per the example descriptions below), the wash cycle was paused and the indicated portion of the withheld hydrophilic surfactant was dosed into the wash liquor. The wash cycle was resumed. After a point in time T3 (as per the example descriptions below), the machine was paused, and the third portion of the withheld hydrophilic surfactant was dosed into the wash liquor. The machine cycle was resumed and proceeded. After the wash cycle, the test fabrics and ballast were rinsed and spun dried twice. After the machine completed the final rinse and spin, the test fabrics were removed from the ballast and dried separately in a machine dryer for 30 minutes at medium heat setting.

Example 1 - Standard detergent loading with a benchmark detergent formulation containing only hydrophilic surfactants - comparative

[0299] The comparative Detergent formulation as per table 3 was added at the start of the wash cycle without withheld portion of hydrophilic surfactants (no dosing). 100% of the detergent formulations were mixed into the wash liquor, the standardized stains, and the ballast fabric were added, and the machine wash cycle was started.

Example 2 - Standard detergent loading - comparative

[0300] Formulation 1 as per table 3 was added at the start of the wash cycle without withheld portion of hydrophilic surfactants (no dosing). 100% of the detergent formulations were mixed into the wash liquor, the standardized stains, and the ballast fabric were added, and the machine wash cycle was started.

Example 3 - Time release dosing

[0301] At the start of the wash cycle, formulation 1 as per table 3 with 50% of the withheld hydrophilic surfactant was added to the machine wash liquor, the standardized stains and the ballast fabric were added, and the machine wash cycle was started. After 5 minutes, the machine was paused and 50% of the withheld hydrophilic surfactant dosed into the wash liquor. The machine cycle resumed. After another 5 minutes, the machine was paused and the remaining 50% of the withheld hydrophilic surfactant was dosed into the wash liquor. The machine cycle resumed and proceeded.

Example 4 - Time release dosing

[0302] At the start of the wash cycle, formulation 1 as per table 3 with 50% of the withheld hydrophilic surfactant was added to the machine wash liquor, the standardized stains and the ballast fabric were added, and the machine wash cycle was started. After 5 minutes, the machine was paused and 100% of the withheld hydrophilic surfactant was dosed into the wash liquor. The machine cycle resumed and proceeded.

Table 3: Compositions for evaluating detergency performance

Detergent Formulation - Comparative		Formulation 1	
Component	wt%	Component	wt%
Va*	6.72	Va*	8.0
Iva*	12.52	IIla	8.0
Ig*	6.24	Ih	8.0
Emery 622	1.80	Emery 622	1.80
NaOH (50%)	0.33	NaOH (50%)	0.33
Sodium Citrate	2.99	Sodium Citrate	2.99
Propylene Glycol	6.08	Propylene Glycol	6.08
Ethanol	1.99	Ethanol	1.99

(continued)

Detergent Formulation - Comparative		Formulation 1	
Component	wt%	Component	wt%
Water	61.33	Water	62.81
*Hydrophilic surfactant Emery® 622: Coconut fatty acid From Sea-Land Chemical Company			

Table 4: Detergency performance of compositions

	(j)	(k)	(l)	(m)
Example 1 Detergent formulation-comparative	254.85	128.79	303.07	686.71
Example 2 - Formulation 1 - comparative	221.48	125.00	294.07	640.55
Example 3 - Time release dosing of formulation 1	295.15	141.55	308.71	745.41
Example 4 - Time release dosing of formulation 1	275.04	135.96	316.98	727.97
(j) ΔE, Sum of all oily stains (k) ΔE, Sum of all enzymatic stains (l) ΔE, Sum of all oxidizable stains (m) ΔE, Sum of all fabrics				

[0303] Throughout all stain types and in sum, examples 3 and 4 according to the invention showed a superior detergency performance (higher ΔE).

[0304] From results summarized in tables 2a, 2b and 4, it can be concluded that the method of laundering articles by dosing of surfactants according to the method of the present invention improves the detergency of surfactant systems.

Claims

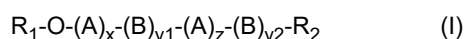
1. A method of laundering articles, the method comprising the steps of:

- providing a wash liquor, said wash liquor comprising a surfactant system S1 that comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant,
- applying said wash liquor to the articles to be laundered and initiating a wash cycle at a point in time T1,
- at a point in time T2 supplying the wash liquor of step b), optionally while pausing the wash cycle, with a surfactant system S2 that comprises at least one hydrophilic surfactant and optionally at least one hydrophobic surfactant, and resuming the wash cycle, and
- if desired repeating step c) one or more times.

2. The method according to claim 1, where the wash liquor applied in step b) has an initial HLD value of -3.5 to +1.5, preferably of -1 to +0.2 and more preferably -1 to +0.1; and the wash liquor obtained in step d), if this is carried out, or obtained in step c), if step d) is not carried out, after surfactant system S2 has been supplied, has a final HLD value of -5 to -0.5, preferably of -5 to -1.5, more preferably of -4 to -2, where the final HLD value is lower by at least 0.2 than the initial HLD value.

3. The method according to any of the preceding claims, wherein the at least one hydrophobic surfactant and at least one hydrophilic surfactant is selected from

- at least one compound of formula (I)



wherein

R₁ is selected from linear or branched C₄-C₂₂-alkyl,
R₂ is selected from H and linear or branched C₁-C₂₂-alkyl,

A is $\text{CH}_2\text{-CH}_2\text{-O}$,

B is $\text{CH}_2\text{-CHR}_3\text{-O}$, wherein R_3 is linear or branched $\text{C}_1\text{-C}_{10}$ -alkyl, preferably methyl,

x is in the range from 0 to 35,

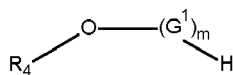
y₁ is in the range from 0 to 60,

y₂ is in the range from 0 to 35,

z is in the range from 0 to 35, and

wherein the sum of $x+y_1+z+y_2$ is at least 2;

b) at least one compound of formula (II),



(II)

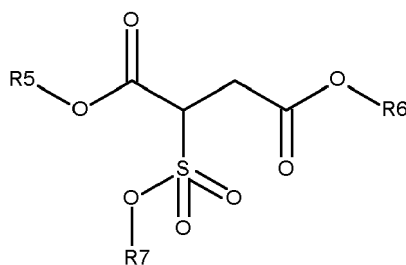
wherein

R_4 is a linear or branched $\text{C}_6\text{-C}_{30}$ -alkyl,

G^1 is a monosaccharide residue having 5 or 6 carbon atoms,

m is on average in the range of 1 to 10;

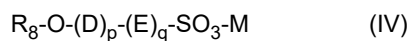
c) at least one compound of formula (III),



(III),

wherein each of R_5 and R_6 is a linear or branched $\text{C}_4\text{-C}_{22}$ -alkyl, or a linear or branched unsaturated aliphatic $\text{C}_4\text{-C}_{22}$ -hydrocarbon radical, and R_7 is a hydrogen atom or alkali metal or an alkaline earth metal cation equivalent,

d) at least one compound of formula (IV)



wherein

R_8 is a linear or branched $\text{C}_6\text{-C}_{22}$ -alkyl,

D denotes $\text{CH}_2\text{-CHR}_9\text{-O}$, wherein R_9 is linear or branched $\text{C}_1\text{-C}_{10}$ -alkyl, preferably methyl,

E denotes $\text{CH}_2\text{-CH}_2\text{-O}$,

p is in the range from 0 to 10,

q is in the range from 0 to 5,

M is H or an alkali metal or ammonium cation,

e) at least one surfactant (V) which is selected from the group consisting of $\text{C}_5\text{-C}_{20}$ -alkylbenzene sulfonic acids and salts thereof;

or mixtures thereof.

4. The method according to claim 3, wherein

the hydrophobic surfactant is selected from the group consisting of

a) at least one compound of formula (I), wherein

- $(y_1 + y_2) = 0$ and $(x + z) \leq 5$; or
- $(x + z) = 0$; or
- $(y_1 + y_2) \neq 0$, $(x + z) \neq 0$ and $(x+z) - (y_1 + y_2) \leq 2$; preferably ≤ 0 ; or
- R_2 is linear or branched C_1 - C_{22} -alkyl;

where the last condition can apply simultaneously with one or more of the first three conditions;

b) at least one compound of formula (II);

c) at least one compound of formula (III), wherein R_5 and R_6 have together at least 14 carbon atoms;

and mixtures thereof;

and wherein

the hydrophilic surfactant is selected from the group consisting of

a) at least one compound of formula (I), wherein

- $(y_1 + y_2) < 3$ and $(x + z) \geq 6$ and R_2 is hydrogen;

c) at least one compound of formula (III), wherein R_5 and R_6 have together at most 12 carbon atoms; wherein preferably R_7 is an alkali metal or an alkaline earth metal cation (equivalent);

d) at least one compound of formula (IV), wherein M is preferably an alkali metal or ammonium cation;

e) at least one compound of formula (V), which is preferably a salt of a C_5 - C_{20} -alkylbenzene sulfonic acid;

and mixtures thereof.

5. The method according to any of claims 3 or 4, wherein

- in compounds (I) R_1 is linear or branched C_4 - C_{18} -alkyl, preferably linear or branched C_8 - C_{18} -alkyl, more preferably linear or branched C_8 - C_{16} -alkyl, even more preferably linear or branched C_{10} - C_{16} -alkyl; or R_1O is derived from a linear or branched C_4 - C_{18} -alkanol, preferably from a linear or branched C_8 - C_{18} -alkanol, more preferably from a linear or branched C_8 - C_{16} -alkanol, even more preferably from a linear or branched C_{10} - C_{16} -alkanol, where the alkanol is in particular selected from 2-propylheptanol, lauryl alcohol, linear or branched tridecyl alcohol, myristyl alcohol, C_{13} - C_{15} oxo alcohols and mixtures thereof; and/or

- in compounds (II) R_4 is a linear or branched C_6 - C_{20} -alkyl, preferably linear or branched C_8 - C_{15} -alkyl; G^1 is selected from the group consisting of ribulose, xylulose, ribose, arabinose, xylose, lyxose, galactose, mannose, rhamnose, glucose and mixtures thereof, preferably from glucose, xylose, arabinose, rhamnose and mixtures thereof and in particular from glucose, xylose and mixtures thereof; and m is from 1.05 to 2.5, preferably m from 1.10 to 1.8, in particular from 1.1 to 1.4 and/or

- in compounds (III) R_5 and R_6 are independently a linear or branched C_6 - C_{12} -alkyl or a linear or branched unsaturated aliphatic C_6 - C_{12} -hydrocarbon radical, preferably a C_6 - C_{10} -alkyl; and R_7 is an alkali metal or an alkaline earth metal cation equivalent, preferably an alkali metal equivalent; and/or

- in compounds (IV) R_8 is C_{10} - C_{16} -alkyl, preferably C_{10} - C_{14} -alkyl; $p = 0$, $q = 2$ to 6 , preferably 2 to 4 ; and M is an alkali metal; and/or

- compounds (V) are the alkali metal salts of C_8 - C_{16} -alkylbenzene sulfonic acids, preferably the alkali metal salts of C_{10} - C_{14} -alkylbenzene sulfonic acids.

6. The method according to any of the preceding claims, wherein one or both of conditions (a) and/or (b) apply:

(a) the surfactant system S1 comprises the one or more one hydrophobic surfactants in a total amount of 45 wt. % to 100 wt. % and the one or more hydrophilic surfactants in a total amount of 0 wt. % to 55 wt. %, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S1; wherein preferably the surfactant system S1 comprises the one or more one hydrophobic surfactants in a total amount of 50 wt. % to 100 wt. % and the one or more hydrophilic surfactants in a total amount of 0 wt. % to 50 wt. %, based on the total

weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S1; and wherein more preferably the surfactant system S1 comprises the one or more one hydrophobic surfactants in a total amount of 55 wt.% to 100 wt.% and the one or more hydrophilic surfactants in a total amount of 0 wt.% to 45 wt.%, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S1; and/or
 5 (b) the surfactant system S2 comprises the one or more one hydrophobic surfactants in a total amount of 0 wt.% to 45 wt.% and the one or more hydrophilic surfactants in a total amount of 55 wt.% to 100 wt.%, based on the total weight of all hydrophilic and hydrophobic surfactants contained in the surfactant system S2; wherein preferably the surfactant system S2 comprises no hydrophobic surfactants.

10 7. The method according to any of the preceding claims, wherein the weight ratio of the overall amount of hydrophobic surfactant(s), as comprised in surfactant system 1 and, if present, in surfactant system 2, to the overall amount of hydrophilic surfactant(s), as comprised in surfactant system 2 and, if present, in surfactant system 1, is in the range of 5:1 to 1:5, preferably from 3:1 to 1:1.5, more preferably from 3:1 to 1:1 and in particular from 2:1 to 1:1.

15 8. The method according to any of the preceding claims, wherein point in time T2 is in the range of 1 second to 15 minutes after T1, preferably 1 minute to 15 minutes after T1, more preferably 2 to 12 minutes after T1.

9. The method according to any of the preceding claims, wherein the wash liquor further comprises water.

20 10. The method according to any of the preceding claims, wherein the wash cycle is carried out at from 25 to 95°C, preferably from 25 to 60°C.

11. A composition comprising

- 25 i) a surfactant system S comprising at least one hydrophobic surfactant and at least one hydrophilic surfactant, and
 ii) optionally additives,

30 wherein the at least one hydrophobic surfactant and at least one hydrophilic surfactant are as defined in any of claims 3 to 5;
 where at least 10% by weight of the hydrophilic surfactant, based on the total weight of the hydrophilic surfactant(s) present in the surfactant system S, is present in a delayed release form.

35 12. The composition according to claim 11, wherein the amount of surfactant system S is in the range of 5 wt% to 90 wt%, based on the total weight of the composition.

40 13. The composition according to any one of claims 11 or 12, wherein additives are selected from the group consisting of chelating agents, enzymes, builders, bleaching agents, fragrances, fillers, anti-static agents, odor capturing agents, fiber protection agents, colour protection agents, soil releasing agents, UV protection agents, anti-pilling agents, viscosity control agents, stabilizers, optical brighteners, soaps, silicon based defoamers, colourants, solvents and mixtures thereof.

14. Use of the composition according to any of claims 11 to 13 for laundering articles.

45 15. A kit of parts comprising at least two parts, where the first part comprises at least one hydrophobic surfactant and optionally at least one hydrophilic surfactant; and the second part comprises at least one hydrophilic surfactant, but no hydrophobic surfactant, where the hydrophobic and the hydrophilic surfactants are preferably as defined in claims 3 to 5; or where the first part comprises surfactant system S1 and the second part comprises surfactant system S2, where surfactant systems S1 and S2 are as defined in any of claims 1 to 8,

50 where the kit of parts is capable of being used in a method for laundering articles according to any of claims 1 to 10; where preferably the first part comprises at least one hydrophobic surfactant, optionally at least one hydrophilic surfactant; and additives, where the additives are preferably as defined in claim 132, and the second part comprises at least one hydrophilic surfactant and optionally one or more additives, where the additives are preferably as defined in claim 13; or where the first part comprises surfactant system S1 and optionally additives, where the additives are preferably as defined in claim 13, and the second part comprises surfactant system S2 and optionally additives, where the additives are preferably as defined in claim 13.



EUROPEAN SEARCH REPORT

Application Number

EP 23 20 7112

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The Hague		26 March 2024	Loiselet-Taisne, S
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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