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(54) **LAUNDRY DETERGENT COMPOSITION**

(57) The present invention relates to a laundry detergent composition having alkyl ether carboxylic acid or a salt thereof in combination with lipase for suppressing foaming during the rinse stage of the laundering process. Moreover, the invention relates to a method for reducing foaming during the rinsing stage.

The present inventors had found that alkyl ether carboxylic acid or a salt thereof in combination with lipase can be used to provide antifoaming benefits by significantly reducing the foam during the rinse cycle while maintaining comparable foam volume during the main wash cycle of the laundering process.

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Description**Field of the invention**

- 5 **[0001]** The present invention provides an alkyl ether carboxylic acid in combination with lipase in a laundry cleaning composition for suppressing foaming.

Background of the invention

- 10 **[0002]** Water is becoming a more and more scarcely available commodity, especially in developing countries, where it is not unusual that people have to walk many kilometres to arrive at a water source. Laundering fabrics, dishwashing and other household cleaning processes, consumes large amounts of water. These are daily chores in which the use of water and a detergent cannot be avoided. There is an increasing need to save water. One way of saving water is to reuse the water and another way is to reduce the amount of water being consumed for various household activities.

- 15 **[0003]** Consumers usually prefer to see a lot of foam while washing as they associate foaming with detergent efficiency. Foam profile is important for laundry detergents, especially those designed for hand washing fabrics, where the appropriate volume and speed of foam formation, retention in the wash and disappearance over one or more rinse cycles are considered key benchmarks of performance by the consumers. High foam is especially desirable during hand washing of fabrics, since the consumer can directly feel and touch the foam generated during the wash cycle and intuitively
20 correlates the high foam volume with effective fabric cleaning.

- [0004]** Paradoxically, while a large volume of foam is desirable during the wash cycle of fabric cleaning, it is nevertheless undesirable during the rinse cycle. If such high foam is still present during rinse, then the consumers immediately infers from it that there may still be surfactant residue on the fabrics and that the fabrics are not yet "clean". In hand washing and in many automatic washing machines, rinsing is repeated till the foam carried over by the wash cycle has reached
25 an acceptably low level. The number of rinses required is dictated by the amount of foam remaining in the rinse water. As water is often a limited resource, especially in hand washing countries, the excess amount of water consumed by multiple rinses reduces the amount of water available for other uses, such as irrigation, drinking, bathing, etc.

- [0005]** Thus, it has been a challenge to provide consumers with a laundry cleaning composition that maintains the initial foam while exhibiting an antifoaming effect during rinse.

- 30 **[0006]** It is common for modern laundry detergent compositions to contain an antifoam material, particularly when intended for use in front loading automatic washing machines. The most common kind of antifoam material used is a silicone oil. Being hydrophobic and water immiscible, such silicones are conventionally provided by the manufacturer in the form of a silicone/silica emulsion. However, this may lead to a problem with regard to the stability of the resulting mixture when trying to incorporate such emulsified antifoams into an aqueous liquid detergent formulation. Additionally,
35 silicone is non-biodegradable and are environmentally less preferred.

- [0007]** Some detergent composition may include a delayed-release amino-silicone based anti-foaming agent that is absorbed onto a carrier or filler to act in the rinsing cycle to reduce or eliminate foam, preferably after two rinse cycles. Such delayed-release amino-silicone are generally cost-prohibitive for most hand-washing consumers. Further, the foam control benefit imparted by such amino silicone based anti-foaming agent may come at the expense of wash foam, i.e.,
40 the wash foam volume can be significantly reduced since the silicone release timing is difficult to control. Inopportune release of the silicone antifoam may lead to significant reduction of wash foam volume, which will give consumer the impression that the detergent composition contains lower surfactant level and is therefore of lower quality or value. In addition to silicone the detergent compositions also include a builder. The builder is generally a carbonate-based builder as phosphate builders are associated with environmental concerns.

- 45 **[0008]** Alkyl ether carboxylic acid and enzymes are known to deliver effective stain removal benefits in detergent compositions.

- [0009]** One such detergent composition is disclosed in WO2017/055205 A1 (Unilever) which is a phosphate free carbonate-built powder detergent formulation having anionic surfactant, alkyl ether carboxylic acid with saturated alkyl chain and protease to effectively remove stains in carbonate build powder detergent formulations having a high fraction
50 of anionic surfactant relative to non-ionic surfactant. The composition includes an alkyl ether carboxylic acid with C₁₂ saturated alkyl chain along with lipase and protease.

- [0010]** WO2016/180552 A1 (Unilever) discloses a detergent composition having 5 wt.% to 50 wt.% surfactant, 0.5 wt.% to 20wt% alkyl ether carboxylic acid dispersant thereof having C₁₆ to C₂₆ carbon chain and 0.0005 wt.% to 2 wt.% protease for providing enhanced stain removal.

- 55 **[0011]** Thus, there is a need for a laundry detergent composition with improved foaming profile characterized by both high wash foam volume and low rinse foam volume as desired by consumers of hand washing habits.

- [0012]** It is therefore an object of the present invention to provide a carbonate-built detergent composition which provides improved foam profile in wash and effective foam suppression during the rinse stage.

[0013] It is another object of the present invention to provide a laundry detergent composition which provides improved foam profile while retaining good stain removal and cleaning benefits.

[0014] It is yet another object of the present invention to provide a laundry detergent composition which provides the dual benefit of good stain removal benefits and good foam suppressing benefits during rinse without the use of additional antifoaming agents.

Summary of the invention

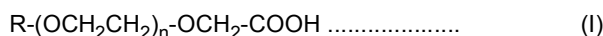
[0015] Surprisingly the combination of specific alkyl ether carboxylic acid or a salt thereof with lipase in a laundry detergent composition, provides antifoaming activity during the rinse stage when the fabric having sebum soil is cleaned with the detergent composition.

[0016] It was found by the present inventors that while washing difficult to remove sebum stains from a fabric with a carbonate-built detergent composition, the presence of specific alkyl ether carboxylic acid along with lipase contributes to suppressing the foam during the rinse cycle, the combination of lipase with specific alkyl ether carboxylic acid also contributes to good foamability along with the anionic surfactant in the washing cycle and good stain removal benefits.

[0017] It is further found that the benefits of antifoaming during the rinse stage is enhanced when the specific alkyl ether carboxylic acid has C₁₆ to C₁₈ monounsaturated linear or branched alkyl chain and having molar number average of ethoxy groups ranging from 5 to 20.

[0018] Accordingly, in a first aspect the present invention provides a laundry detergent composition for treating a fabric article soiled with sebum from human skin, the composition comprising:

i. an alkyl ether carboxylic acid of the following structure (I) or a salt thereof:



wherein:

R = C₁₆ to C₂₀ linear or branched saturated carbon chain; or, a C₁₆ to C₂₀ linear or branched mono-unsaturated carbon chain;

n = molar number average of ethoxy groups, and when R is saturated n is selected from 10 to 30 and when R is mono-unsaturated, n is selected from 5 to 20.

ii. a lipase enzyme;

iii. from 5 wt.% to 40 wt.% sodium carbonate; and,

iv. from 0 wt.% to 4 wt.% phosphate builder.

[0019] According to a second aspect of the present invention disclosed is a method for reducing the foaming at the rinse stage during a washing cycle, the method comprising the steps of:

i. contacting a textile article soiled with sebum from human skin with a laundry detergent composition comprising alkyl ether carboxylic acid or a salt thereof in combination with a lipase during a main wash cycle of a laundering process;

ii. rinsing the textile article with water; and,

iii. optionally drying the textile article.

[0020] As used herein, "foam" indicates a non-equilibrium dispersion of gas bubbles in a relatively smaller volume of a liquid. The terms like "suds", "foam" and "lather" can be used interchangeably within the meaning of the present invention.

[0021] As used herein, "foam profile" refers to the properties of a detergent composition relating to foam character during the wash and rinse cycles. The foam profile of a detergent composition includes, but is not limited to, the speed of foam generation upon dissolution in the laundering liquor, the volume and retention of foam in the wash cycle, and the volume and disappearance of foam in the rinse cycle. Preferably, the foam profile includes the wash foam height and rinse foam height as specifically defined by the testing methods disclosed hereinafter in the examples. It may further include additional foam-related parameters, such as foam stability measured during the washing cycle and the like.

[0022] As used herein, the term "detergent composition" includes granular, powder, liquids, tablets, bars or gel composition. Preferably the detergent composition is a laundry detergent composition.

[0023] "Antifoaming benefits" means the suppression of the foam during the rinse stage of laundering textile article with a detergent composition, especially a laundry detergent composition and where the composition retains its ability to provide satisfactory foam profile during the washing or the pre-rinse stage, but which requires lesser than the usual

number of rinse cycles for the foam to subside.

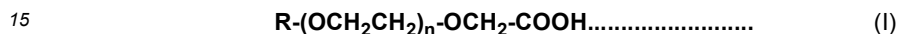
Detailed description of the invention

- 5 **[0024]** According to a first aspect of the present invention disclosed is a laundry detergent composition comprising an alkyl ether carboxylic acid, a lipase enzyme and sodium carbonate builder.

Alkyl ether carboxylic acid

- 10 **[0025]** In the context of the current invention alkyl ether carboxylic acid are not included as anionic surfactants. The percentage weight of alkyl ether carboxylic acid is calculated as the protonated form, $R-(OCH_2CH_2)_n-OCH_2COOH$. They may be used as salt version for example sodium salt, or amine salt.

[0026] The alkyl ether carboxylic acid of the present invention is of the following structure (I)



[0027] The R group in the alkyl ether carboxylic acid is a C_{16} to C_{20} linear or branched saturated carbon chain. The R group is preferably a C_{16} , C_{18} or C_{20} linear or branched saturated carbon chain. More preferably the R group is a C_{16} or C_{18} linear or branched saturated carbon chain or a mixture thereof.

- 20 **[0028]** Alternately, the R group in the alkyl ether carboxylic acid is a C_{16} to C_{20} linear or branched mono-unsaturated carbon chain. The R group is preferably a C_{16} , C_{18} or C_{20} linear or branched mono-saturated carbon chain. More preferably the R group is a C_{16} or C_{18} linear mono-unsaturated carbon chain or a mixture thereof.

[0029] The alkyl chain may be linear or branched, preferably it is linear. The alkyl chain may be saturated or mono-unsaturated, preferably unsaturated.

- 25 **[0030]** The alkyl chain is preferably aliphatic and linear and may be selected from: $CH_3(CH_2)_{15}$; $CH_3(CH_2)_{16}$; $CH_3(CH_2)_{17}$; $CH_3(CH_2)_{18}$; and $CH_3(CH_2)_{19}$. The alkyl chain is preferably selected from $CH_3(CH_2)_{15}$; $CH_3(CH_2)_{17}$ or mixtures thereof. The alkyl ether carboxylic acid is most preferably of the structure selected from $CH_3(CH_2)_{15}(OCH_2CH_2)_{20}OCH_2COOH$, $CH_3(CH_2)_{17}(OCH_2CH_2)_{20}OCH_2COOH$ or a mixture thereof.

- 30 **[0031]** The alkyl chain may contain one double bond, the double bond may be cis or trans, preferably the double bond is a cis-double bond. Preferred examples of alkyl chain with single double bond are $CH_3(CH_2)_7CH=CH(CH_2)_8$; $CH_3(CH_2)_5CH=CH(CH_2)_8$ or mixtures thereof.

[0032] Most preferably the alkyl chain is selected from oleic, elaidic, palmitic, stearic and mixtures thereof.

- 35 **[0033]** In the provided structure (I) of the alkyl ether carboxylic acid, n represents the molar number average of ethoxy groups. The value of n is selected from 10 to 30 when the R group is a saturated carbon chain and when R is monounsaturated, n is selected from 5 to 20, preferably from 8 to 20, still preferably from 9 to 20, further preferably from 10 to 20.

[0034] The alkyl ether carboxylic acid when saturated is most preferably selected from a $CH_3(CH_2)_{15}(OCH_2CH_2)_{20}OCH_2COOH$, $CH_3(CH_2)_{17}(OCH_2CH_2)_{20}OCH_2COOH$ or mixture thereof.

- 40 **[0035]** The alkyl ether carboxylic acid when monounsaturated is most preferably selected from the structure $CH_3(CH_2)_5CH=CH(CH_2)_8(OCH_2CH_2)_{10}OCH_2COOH$, $CH_3(CH_2)_7CH=CH(CH_2)_8(OCH_2CH_2)_{10}OCH_2COOH$ or a mixture thereof.

[0036] Without being limited by theory it is believed that antifoaming benefits is greatly enhanced in the presence of alkyl ether carboxylic acid with C_{16} to C_{18} linear or branched mono-unsaturated carbon chain or salt thereof, this is because said alkyl ether carboxylic acid has a matching chain length to the fats present in sebum which contains considerable amounts of C_{16} and C_{18} mono unsaturated alkyl chains for example sapeienic acid ($C_{16}:1$).

- 45 **[0037]** Commercially alkyl ether carboxylic acid are available from Kao (Akypo®), Sassol (Marlowet®) Huntsman (Empicol®) and Clariant (Emulsogen®).

[0038] In a solid cleaning composition, the alkyl ether carboxylic acid or a salt thereof is preferably added to the slurry before granulation of the detergent powder. Alternatively, it may be separately granulated and post dosed or sprayed onto the finished powder.

- 50 **[0039]** For liquids, the alkyl ether carboxylic acid or a salt thereof is preferably pre-mixed with another surfactant before dosing and mixing into the detergent composition.

- [0040]** Preferably the laundry detergent composition according to the present invention comprises from 0.2 wt.% to 20 wt.% alkyl ether carboxylic acid having a structure represented by the general structure (I) or a salt thereof. Preferably the laundry detergent composition comprises at least 0.3 wt.% alkyl ether carboxylic acid based on the weight of the laundry detergent composition, still preferably at least 0.5 wt.%, still preferably at least 0.8 wt.%, most preferably at least 1 wt.%, but typically not more than 8 wt.%, still preferably not more than 6 wt.%, more preferably not more than 5 wt.%, most preferably not more than 4 wt.% alkyl ether carboxylic acid or a salt thereof in the detergent composition.

Lipase

[0041] The detergent composition according to the invention include a lipase enzyme. Lipase (also known as esterase) is an enzyme which catalyses hydrolysis of ester bonds of edible fats and oils, i.e. triglycerides, into free fatty acids, mono- and diglycerides and glycerol. It is believed that the primary function of lipase is to reduce build-up of sebum. The use of lipase is of special interest for low temperature washes as then oils and fats are in the solid state and therefore more difficult to remove. It is also believed that the action of lipase is not manifested during the main-wash, but in between washes. It is believed that first the lipase gets adsorbed on top of soil during main-wash, but its action is inhibited by surfactants. During the rinse stage, lipase remains adsorbed and degrades the soil matrix. Lipase is also suitable for detergent compositions that contain higher amount of anionic surfactants, typically 20 to 40 wt%. Lipase is also believed to remove difficult stains like tomato oil, pasta sauce, pesto, motor oil, colourless oils like olive oil and corn oil. It is believed that lipase continues its action during the drying stage forming fatty acids, diglycerides and monoglycerides.

[0042] Cleaning lipases are discussed in *Enzymes in Detergency* edited by Jan H. Van Ee, Onno Misset and Erik J. Baas (1997 Marcel Dekker, New York). Cleaning lipases are preferably active at alkaline pH in the range 7 to 11, most preferably they have maximum activity in the pH range 8 to 10.5. The lipase may be selected from lipase enzymes in E.C. class 3.1, 3.2 or a combination thereof.

[0043] Preferably the cleaning lipases selected is a Triacylglycerol lipases (E.C. 3.1.1.3). Suitable triacylglycerol lipases can be selected from variants of the *Humicola lanuginosa* (*Thermomyces lanuginosus*) lipase. Other suitable triacylglycerol lipases can be selected from variants of *Pseudomonas* lipases, e.g., from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*, *Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* 25 (WO 96/12012), *Bacillus* lipases, e.g., from *B. subtilis* (Dartois et al. (1993), *Biochimica et Biophysica Acta*, 1131,253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

[0044] Further examples of EC 3.1.1.3 lipases include those described in WIPO publications WO 00/60063, WO 99/42566, WO 02/062973, WO 97/04078, WO 97/04079 and US 5,869,438. Preferred lipases are produced by *Absidia reflexa*, *Absidia corymbifera*, *Rhizomucor miehei*, *Rhizopus deleman* *Aspergillus niger*, *Aspergillus tubigensis*, *Fusarium oxysporum*, *Fusarium heterosporum*, *Aspergillus oryzae*, *Penicillium camembertii*, *Aspergillus foetidus*, *Aspergillus niger*, *Thermomyces lanuginosus* (synonym: *Humicola lanuginosa*) and *Landerina penisapora*, particularly *Thermomyces lanuginosus*.

[0045] Certain preferred lipases are supplied by Novozymes and includes those under the tradenames of Lipolase®, Lipolase Ultra®, Lipoprime®, Lipoclean® and Lipex® (registered tradenames of Novozymes) and LIPASE P "AMANO®" available from Areario Pharmaceutical Co. Ltd., Nagoya, Japan, AMANO-CES®, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from Amersham Pharmacia Biotech., Piscataway, New Jersey, U.S.A. and Diosynth Co., Netherlands, and other lipases such as *Pseudomonas gladioli*.

[0046] LIPEX® is particularly preferred, and LIPEX® 100 TB is further particularly preferred. The activity of commercial lipase is commonly expressed as Lipase Units or LU. Different lipase preparations may have different activities. For fungal lipases these may range from 2,000 to 2,000,000 LU per gram. The activity may also be represented as FIP units/g or FCC III LU/g. One of these new Lipase Units is equivalent to ten of the old LU, or 1,000 FIP units/g = 10,000 LU/g.

[0047] Preferred compositions include lipase having 5 to 20000 LU/g. In order to prevent accidents and to alleviate safety concerns, commercial lipases are always coated with an inert material. Therefore, commercial lipases that are used for detergent powders, bars and tablets are in granular form containing very low amount of active lipase and balance of adjunct materials. The granulates contain lipase concentrate, inorganic salt, binders and coating materials. They are free flowing so that there is no lumping, and the granulates dissolve faster. On the other hand, lipases fit for liquid detergents are available in liquid form. An example is LIPEX® 100 L.

[0048] Additional useful lipases are described in WIPO publications WO 02062973, WO 2004/101759, WO 2004/101760 and WO 2004/101763. In one embodiment, suitable lipases include the "first cycle lipases" described in WO 00/60063 and U.S. Patent 6,939,702 B1, preferably a variant of SEQ ID No. 2, more preferably a variant of SEQ ID No. 2 having at least 90% homology to SEQ ID No. 2 comprising a substitution of an electrically neutral or negatively charged amino acid with R or K at any of positions 3, 224, 229, 231 and 233, with a most preferred variant comprising T23 IR and N233R mutations, such most preferred variant being sold under the tradename Lipex® (Novozymes).

[0049] The aforementioned lipases can be used in combination (any mixture of lipases can be used). Suitable lipases can be purchased from Novozymes, Bagsvaerd, Denmark; Areario Pharmaceutical Co. Ltd., Nagoya, Japan; Toyo Jozo Co., Tagata, Japan; Amersham Pharmacia Biotech., Piscataway, New Jersey, U.S.A.; Diosynth Co., Oss, Netherlands and/or made in accordance with the examples contained herein. Lipase with reduced potential for odour generation and a good relative performance, are particularly preferred, as described in WO2007/087243. These include lipoclean® (Novozyme).

[0050] Preferably the laundry detergent composition according to the present invention comprises from 0.0001 wt.% to 0.1 wt.% of pure enzyme of lipase. Preferably the laundry detergent composition comprises at least 0.0005 wt.%, still

preferably at least 0.001 wt.%, still preferably at least 0.002 wt.%, most preferably at least 0.005 wt.%, but typically not more than 0.05 wt.%, still preferably not more than 0.03 wt.%, most preferably not more than 0.01 wt.%.

Laundry detergent composition

[0051] The laundry detergent formulation is preferably a non-phosphate laundry detergent formulation, i.e., contains less than 4 wt.% of phosphate. In this art the term 'phosphate' includes diphosphate, triphosphate, and phosphonate species. Powder laundry detergent formulations are predominantly carbonate built, i.e. the weight% of sodium carbonate is greater than the weight % sum of other builder ingredient present, preferably the weight% level of other builder materials is less than 30%, more preferably less than 15 wt% of the weight% level of sodium carbonate. Powders, should preferably give an in-use pH of from 9.5 to 11.

[0052] The detergent composition may be a liquid laundry detergent composition or a solid laundry detergent composition. Preferably when the detergent composition is a liquid laundry detergent composition it has a pH from 5 to 11, preferably from pH 6.5 to 8.5, most preferably from pH 6.5 to 8. Preferably when the detergent composition is a solid laundry detergent composition it has a pH from 5 to 11, preferably from pH 8.0 to 10.5, most preferably from pH 9.5 to 10.5.

Surfactant

[0053] The laundry detergent composition preferably comprises an anionic charged surfactant (which includes a mixture of the same). The composition comprises from 4 wt.% to 50 wt.% surfactant, preferably from 6 wt.% to 50 wt.%, more preferably from 7 wt.% to 30 wt.% surfactant in the composition.

[0054] The formulation may contain non-ionic surfactant, preferably the weight fraction of non-ionic surfactant to anionic surfactant is from 0 to 0.3, preferably 0 to 0.1.

[0055] Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher alkyl radicals.

[0056] Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈ to C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉ to C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀ to C₁₅ benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum.

[0057] The anionic surfactant is preferably selected from: linear alkyl benzene sulphonate (LAS); alkyl sulphates; alkyl ether sulphates; soaps; alkyl (preferably methyl) ester sulphonates, and mixtures thereof.

[0058] The most preferred anionic surfactants are selected from: linear alkyl benzene sulphonate; alkyl sulphates; alkyl ether sulphates and mixtures thereof. Preferably the alkyl ether sulphate is a C₁₂ to C₁₄ n-alkyl ether sulphate with an average of 1 to 3EO (ethoxylate) units. Sodium lauryl ether sulphate is particularly preferred (SLES). Preferably the linear alkyl benzene sulphonate is a sodium C₁₁ to C₁₅ alkyl benzene sulphonates. Preferably the alkyl sulphates is a linear or branched sodium C₁₂ to C₁₈ alkyl sulphates. Sodium dodecyl sulphate is particularly preferred, (SDS, also known as primary alkyl sulphate). Preferably the anionic surfactant is selected from LAS, SLES or mixtures thereof.

[0059] The amount of anionic surfactant in the laundry detergent composition is from 4 wt.% to 50 wt.%, more preferably from 5 wt.% to 20 wt.%. It is preferable in the composition that LAS is the dominant anionic surfactant present. In a carbonate-built powder detergent composition, it is preferable in the composition that LAS is the dominant anionic surfactant present, preferably more than 90wt% of the anionic surfactant is LAS.

[0060] Suitable non-ionic detergent compounds which may be used include, in particular, the reaction products of compounds having an aliphatic hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids or amides, especially ethylene oxide either alone or with propylene oxide. Preferred non-ionic detergent compounds are the condensation products of aliphatic C₈ to C₁₈ primary or secondary linear or branched alcohols with ethylene oxide. Most preferably the non-ionic detergent compound is the alkyl ethoxylated non-ionic surfactant is a C₈ to C₁₈ primary alcohol with an average ethoxylation of 7EO to 9EO units. Preferably the surfactants used are saturated.

Builders

[0061] The laundry detergent composition according to the present invention includes 5 wt.% to 40 wt.% sodium carbonate, preferably from 10 wt.% to 20 wt.% sodium carbonate.

[0062] Preferably the detergent composition includes from 0 wt.% to 4 wt.% phosphate builder.

[0063] Other builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

[0064] Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium

tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

[0065] Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

[0066] Examples of calcium ion-exchange builder materials include the various types of water insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0, 384,070. Preferably the detergent composition comprises from 0 wt.% to 8 wt.% of zeolite builder.

[0067] The composition may also contain 0 to 65% of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.

[0068] Zeolite and carbonate (including bicarbonate and sesquicarbonate) are preferred builders for powder detergent compositions.

[0069] The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 5 wt.%. Aluminosilicates are materials having the general formula:



where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

[0070] Alternatively, or additionally to the aluminosilicate builders, other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst) may be present. Preferably the detergent composition includes 0 wt.% to 8 wt.% sodium silicates.

[0071] Detergent composition according to the present invention includes from 5 wt.% to 45 wt.% inorganic salt selected from the group consisting of alkali metal salt of chlorides, alkali metal carbonates or mixtures thereof. Preferably the inorganic salts present in the detergent composition includes but is not limited to sodium chloride, sodium carbonate, calcium carbonate or mixtures thereof.

Antifoam

[0072] The detergent composition according to the present invention may preferably include antifoam or suds suppressing material. Suitable antifoam materials are preferably in granular form for use in powder composition, such as those described in EP 266863A (Unilever). Preferably antifoam materials may be selected from silicone oil, petroleum jelly, hydrophobic silica and fatty acids, more preferably silicone oil and fatty acids. Antifoam may be present in an amount up to 5% by weight of the composition. The detergent composition according to the present invention includes from 0 wt.% to 5 wt.% antifoam, preferably 0.5 wt.% to 5 wt.%. Preferably no antifoam is required in the composition of the present invention.

Other ingredients

Fluorescent Agent:

[0073] The laundry detergent composition may preferably comprise a fluorescent agent (optical brightener). Fluorescent agents are well known, and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 wt.% to 2 wt.%, more preferably 0.01 wt.% to 0.1 wt.%.

[0074] Preferred classes of fluorescer are Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[1, 2-d]triazole, disodium 4,4'- bis([(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino)stilbene-2-2' disulfonate, disodium 4,4'-bis([(4-anilino-6-morpholino-1, 3,5-triazin-2-yl)]amino) stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl.

Perfume:

[0075] Preferably the composition comprises a perfume. Many suitable examples of perfumes are provided in the

CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

[0076] It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components.

[0077] In perfume mixtures preferably 15 to 25 wt.% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

[0078] The perfume materials include free perfume, perfume microcapsules or combinations thereof. As is known in the art, free perfumes and perfume microcapsules provide the consumer with perfume hits at different points during the wash cycle. It is particularly preferred that the compositions of the present invention comprise a combination of both free perfume and perfume microcapsules.

[0079] Preferably the compositions of the present invention comprise 0.001 wt.% to 10 wt.% perfume materials, more preferably 0.1 wt.% to 5 wt.% perfume materials, most preferably 0.1 wt.% to 3 wt.% perfume materials.

[0080] Useful perfume components may include materials of both natural and synthetic origin. They include single compounds and mixtures. Specific examples of such components may be found in the current literature, e.g., in Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA). These substances are well known to the person skilled in the art of perfuming, flavouring, and/or aromatizing consumer products.

[0081] The compositions of the present invention preferably comprise 0.05 wt.% to 10 wt.%, more preferably 0.1 wt.% to 8 wt.%, most preferably 0.1 wt.% to 5 wt.% free perfume.

[0082] Particularly preferred perfume components are blooming perfume components and substantive perfume components. Blooming perfume components are defined by a boiling point less than 250°C and a LogP or greater than 2.5. Substantive perfume components are defined by a boiling point greater than 250°C and a LogP greater than 2.5. Boiling point is measured at standard pressure (760 mm Hg). Preferably a perfume composition will comprise a mixture of blooming and substantive perfume components. The perfume composition may comprise other perfume components.

[0083] It is commonplace for a plurality of perfume components to be present in a free oil perfume composition. In the compositions for use in the present invention it is envisaged that there will be three or more, preferably four or more, more preferably five or more, most preferably six or more different perfume components. An upper limit of 300 perfume components may be applied.

[0084] The compositions of the present invention preferably comprise 0.05 wt.% to 10 wt.%, more preferably 0.1 wt.% to 8 wt.%, even more preferably 0.1 wt.% to 5 wt.% perfume microcapsules and most preferably 0.05 wt.% to 4 wt. % perfume microcapsules. The weight of microcapsules is of the material as supplied.

[0085] When perfume components are encapsulated, suitable encapsulating materials, may comprise, but are not limited to; aminoplasts, proteins, polyurethanes, polyacrylates, polymethacrylates, polysaccharides, polyamides, polyolefins, gums, silicones, lipids, modified cellulose, polyphosphate, polystyrene, polyesters or combinations thereof. Particularly preferred materials are aminoplast microcapsules, such as melamine formaldehyde or urea formaldehyde microcapsules.

[0086] Perfume microcapsules of the present invention can be friable microcapsules and/or moisture activated microcapsules. By friable, it is meant that the perfume microcapsule will rupture when a force is exerted. By moisture activated, it is meant that the perfume is released in the presence of water. The compositions of the present invention preferably comprise friable microcapsules. Moisture activated microcapsules may additionally be present. Examples of microcapsules which can be friable include aminoplast microcapsules.

[0087] Perfume components contained in a microcapsule may comprise odiferous materials and/or pro-fragrance materials.

[0088] Particularly preferred perfume components contained in a microcapsule are blooming perfume components and substantive perfume components. Blooming perfume components are defined by a boiling point less than 250°C and a LogP greater than 2.5. Substantive perfume components are defined by a boiling point greater than 250°C and a LogP greater than 2.5. Boiling point is measured at standard pressure (760 mm Hg). Preferably a perfume composition will comprise a mixture of blooming and substantive perfume components. The perfume composition may comprise other perfume components.

[0089] It is commonplace for a plurality of perfume components to be present in a microcapsule. In the compositions for use in the present invention it is envisaged that there will be three or more, preferably four or more, more preferably five or more, most preferably six or more different perfume components in a microcapsule. An upper limit of 300 perfume components may be applied.

[0090] The microcapsules may comprise perfume components and a carrier for the perfume ingredients, such as zeolites or cyclodextrins.

Polymers:

[0091] The composition may comprise one or more further polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

Further Enzymes:

[0092] One or more further enzymes are preferably present in a laundry composition of the invention and when practicing a method of the invention.

[0093] Preferably the level of each further enzyme in the laundry composition of the invention is from 0.0001 wt.% to 0.1 wt.% protein.

[0094] The further enzyme is preferably selected from: amylases, mannanases, proteases; and, cellulases, most preferably amylases and proteases.

[0095] Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Shading dyes:

[0096] Shading dyes are preferably present in the formulation at a level from 0.002 wt.% to 0.2 wt.%.

[0097] Dyes are described in Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments, (H Zollinger, Wiley VCH, Zurich, 2003) and, Industrial Dyes Chemistry, Properties Applications. (K Hunger (ed), Wiley-VCH Weinheim 2003).

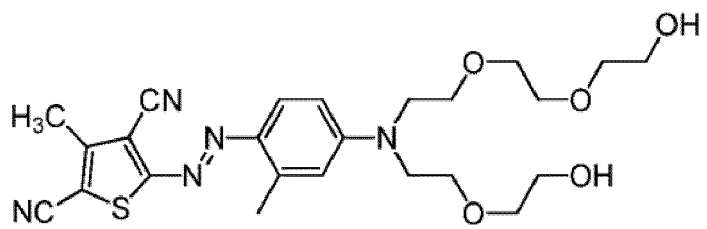
[0098] Shading dyes for use in laundry detergents preferably have an extinction coefficient at the maximum absorption in the visible range (400nm to 700nm) of greater than 5000 L mol⁻¹ cm⁻¹, preferably greater than 10000 L mol⁻¹ cm⁻¹. The dyes are blue or violet in colour.

[0099] Preferred shading dye chromophores are azo, azine, anthraquinone, and triphenylmethane. Azo, anthraquinone, phthalocyanine and triphenylmethane dyes preferably carry a net anionic charged or are uncharged. Azine preferably carry a net anionic or cationic charge.

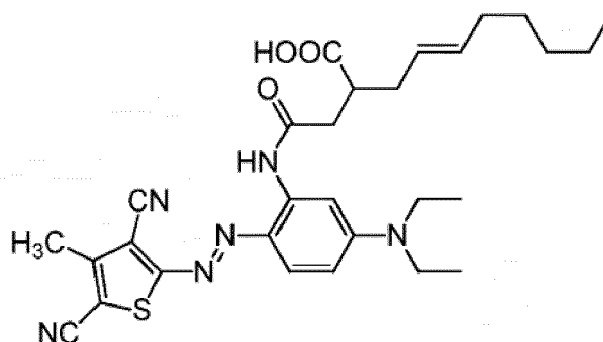
[0100] Blue or violet shading dyes deposit to fabric during the wash or rinse step of the washing process providing a visible hue to the fabric. In this regard the dye gives a blue or violet colour to a white cloth with a hue angle of 240 to 345, more preferably 250 to 320, most preferably 250 to 280. The white cloth used in this test is bleached non-mercerised woven cotton sheeting.

[0101] Shading dyes are discussed in WO2005/003274, WO2006/032327(Unilever), WO 2006/032397 (Unilever), WO2006/045275 (Unilever), WO06/027086 (Unilever), WO 2008/017570 (Unilever), WO 2008/141880 (Unilever), WO2009/132870 (Unilever), WO 2009/141173 (Unilever), WO 2010/099997 (Unilever), WO 2010/102861 (Unilever), WO 2010/148624 (Unilever), WO2008/087497 (P&G), WO2011/011799 (P&G), WO2012/054820 (P&G), WO2013/142495 (P&G), and WO2013/151970 (P&G).

[0102] Mono-azo dyes preferably contain a heterocyclic ring and are most preferably thiophene dyes. The mono-azo dyes are preferably alkoxyated and are preferably uncharged or anionically charged at pH=7. Alkoxyated thiophene dyes are discussed in WO/2013/142495 and WO/2008/087497. Preferred examples of thiophene dyes are shown below:

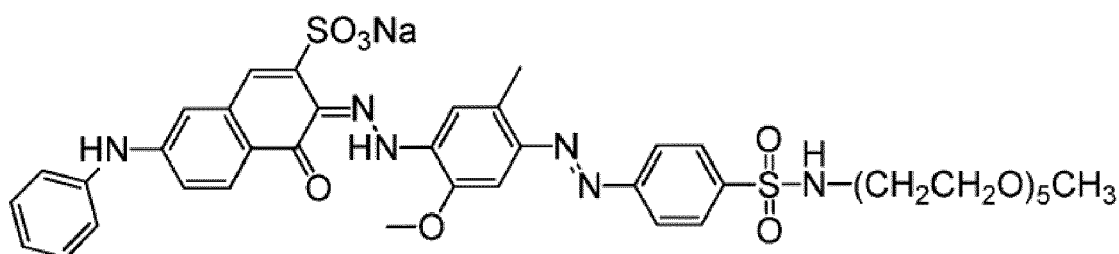


and,

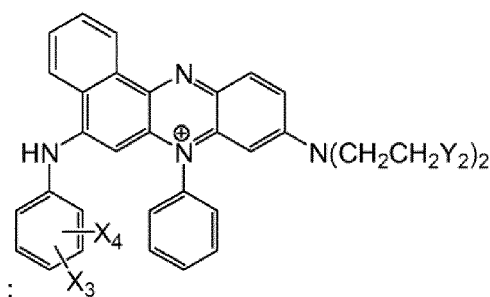


[0103] Bis-azo dyes are preferably sulphonated bis-azo dyes. Preferred examples of sulphonated bis-azo compounds are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, Direct Violet 66, direct violet 99 and alkoxyated versions thereof. Alkoxyated bis-azo dyes are discussed in WO2012/054058 and WO2010/151906.

[0104] An example of an alkoxyated bis-azo dye is:



[0105] Azine dye are preferably selected from sulphonated phenazine dyes and cationic phenazine dyes. Preferred examples are acid blue 98, acid violet 50, dye with CAS-No 72749-80-5, acid blue 59, and the phenazine dye selected from



wherein:

X_3 is selected from: -H; -F; -CH₃; -C₂H₅; -OCH₃; and, -OC₂H₅;

X_4 is selected from: -H; -CH₃; -C₂H₅; -OCH₃; and, -OC₂H₅;

Y_2 is selected from: -OH; -OCH₂CH₂OH; -CH(OH)CH₂OH; -OC(O)CH₃; and, C(O)OCH₃.

[0106] The shading dye is present in the composition in range from 0.0001 wt.% to 0.5 wt.%, preferably 0.001 wt.% to 0.1 wt.%. Depending upon the nature of the shading dye there are preferred ranges depending upon the efficacy of the shading dye which is dependent on class and particular efficacy within any particular class. As stated above the shading dye is a blue or violet shading dye. A mixture of shading dyes may be used.

[0107] The dyes are listed according to Colour Index (Society of Dyers and Colourists /American Association of Textile Chemists and Colorists) classification.

[0108] For ease of use it is preferred if the carbonate-built powder detergent formulations are present in 0.5 Kg to 5

Kg packs.

[0109] According to a second aspect of the present invention disclosed is a method for suppressing the foam at the rinse stage during a washing cycle, the method comprising the steps of:

- i. contacting a textile article soiled with sebum from human skin with a detergent composition comprising alkyl ether carboxylic acid or salt thereof in combination with a lipase during a main wash cycle of a laundering process;
- ii. rinsing the textile article with water; and,
- iii. optionally drying the textile article.

[0110] Preferably the textile article is soiled with sebum from adult human skin. Preferably the method according to the second aspect reduces the foaming at the rinse stage during laundering such that the rinsing stage involves less than 3 rinses, preferably less than 2 rinses and most preferably involves a single rinse step.

Examples

Example 1:

[0111] Two powder detergent compositions were prepared having the formulation as provided in table 1 below.

Table 1

Ingredient	Ex A	Ex 1
Linear alkyl benzene sulfonate	13.5	13.5
Alkyl Ether Carboxylate [#]	0.0	1.0
Sodium Chloride	37.7	36.6
Light soda ash	27.0	27.0
Calcite	14.0	14.0
Lipase granule [*]	0.0	0.1
Minors (including fluorescer, shading dye, perfume & flow aids) and moisture	upto 100	upto 100
[*] Lipase granule contained Lipex 100T a lipid esterase (E.C. 3.1.1.3) from Novozymes. The detergent composition contained 0.0019wt% pure enzyme. [#] mixture of CH ₃ (CH ₂) ₁₅ (OCH ₂ CH ₂) ₂₀ OCH ₂ COOH and CH ₃ (CH ₂) ₁₇ (OCH ₂ CH ₂) ₂₀ OCH ₂ COOH in a C ₁₆ to C ₁₈ ratio of 0.4.		

Panel testing:

[0112] 8 female adult consumers were given a white (cotton/polyester) shirt and were asked to give it to their spouse for wearing it for one day at work. The consumers hand washed the shirts using the comparative detergent powder (Ex A) according to their routine washing protocol, then rinsed and dried them. The washed shirt was then reworn.

[0113] This process was repeated 10 times. After the 1st, 5th and the 10th wear the dirty shirt collar were scored by 15 trained panelists under controlled lighting conditions. The score was on a 10-point scale, where 0 was completely clean and 10 completely filthy. A difference of 1 unit on the scale is visible. The % cleaning of the collar was calculated using the formula given herein below:

$$\% \text{ cleaning} = 100 * \frac{\text{score (before wash)} - \text{score (after wash)}}{\text{score (before wash)}}$$

[0114] The experiment was repeated for detergent powder of Example 1. The average %cleaning values obtained for both the detergent powder compositions were recorded and are given in the table 2 below.

Table 2

	%cleaning		Foam at rinse stage	
Wash-wear cycle	Detergent powder Ex A	Detergent powder Ex 1	Detergent powder Ex A	Detergent powder Ex 1
1	78	87	No noticeable change	No noticeable change
5	73	82	No noticeable change	No noticeable change
10	73	83	No noticeable change	Considerable foam reduction (6 out of 8 consumers)

[0115] It is clear from the above table 2 that the cleaning performance of the detergent composition according to the present invention (Ex 1) is significantly higher than that of the composition according to the comparative example (Ex A). After the 10th wash 6 out of 8 consumers reported that considerably less foam was noticeable upon rinsing the shirt washed with the detergent powder according to the present invention as compared to the reference, Ex A.

[0116] The inventors of the present invention discovered surprisingly and unexpectedly that the use of a combination of specific alkyl ester carboxylic acid and lipase in the detergent composition for treating fabric soiled with sebum from human skin has a significant impact in suppressing the foam at the rinse stage.

Claims

1. A laundry detergent composition for treating textile article soiled with sebum from human skin, the composition comprising:

i. an alkyl ether carboxylic acid of the following structure (I) or a salt thereof;



wherein;

R = C₁₆ to C₂₀ linear or branched saturated carbon chain; or,
a C₁₆ to C₂₀ linear or branched monounsaturated carbon chain;
n = molar number average of ethoxy groups, and when R is saturated n is selected from 10 to 30 and when R is monounsaturated, n is selected from 5 to 20.

ii. a lipase enzyme;
iii. from 5 wt.% to 40 wt.% sodium carbonate; and,
iv. from 0 wt.% to 4 wt.% phosphate builder.

2. A detergent composition according to claim 1 wherein the R group of the alkyl ether carboxylic acid is C₁₆ to C₁₈ linear or branched monounsaturated carbon chain.

3. A detergent composition according to claim 1 or 2 wherein the R group of the alkyl ether carboxylic acid has a mixture of C₁₆ and C₁₈ linear monounsaturated carbon chain.

4. A detergent composition according to claim 1 wherein the R group of the alkyl ether carboxylic acid is C₁₆ to C₁₈ linear or branched saturated carbon chain, preferably a mixture of C₁₆ and C₁₈ linear saturated carbon chain.

5. A detergent composition according to claim 1 wherein the composition comprises from 0wt% to 8wt% zeolite builder.

6. A detergent composition according to claim 1 wherein the composition from 0wt% to 8wt% sodium silicate.

7. A detergent composition according to any one of the preceding claims comprising from 5 wt.% to 45 wt.% inorganic

salt selected from the group consisting of alkali metal salt of chlorides, alkali metal carbonates or mixtures thereof.

8. A detergent composition according to any one of the preceding claims wherein the lipase is present in an amount ranging from 0.0001 wt.% to 0.1 wt % of pure enzyme.

9. A detergent composition according to any one of the preceding claims wherein the composition comprises an anionic surfactant.

10. A detergent composition according to claim 9 wherein the anionic surfactant is selected from LAS, SLES or mixtures thereof.

11. A detergent composition according to claim 9 or 10 wherein anionic surfactant is present in an amount ranging from 4 wt.% to 50 wt.%, preferably from 5 wt.% to 20 wt.%.

12. A detergent composition according to any one of the preceding claims wherein the amount of an alkyl ether carboxylic acid or the salt thereof is present in an amount ranging from 0.2 wt.% to 20 wt.%, more preferably from 0.5 wt.% to 4 wt.%.

13. A detergent composition according to any one of the preceding claims wherein at 1wt% dilution in de-ionised water at 25°C, the solid detergent composition has an equilibrium pH in the range from 5 to 11, preferably from pH 8.0 to 10.5, most preferably from pH 9.5 to 10.5.

14. A method for reducing the foaming at the rinse stage during a washing cycle, the method comprising the steps of:

- i. contacting a textile article soiled with sebum from human skin with a laundry detergent composition comprising alkyl ether carboxylic acid or a salt thereof in combination with a lipase during a main wash cycle of a laundering process;
- ii. rinsing the textile article with water; and,
- iii. optionally drying the textile article.

15. A method for reducing the foaming at the rinse stage of the laundering process wherein the rinsing stage involves less than 3 rinses.



EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2016/198263 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC D/B/A UNILEVER [US]) 15 December 2016 (2016-12-15) * claims 1-6,8-11 * * page 3, line 9 - page 6, line 31 * * page 9, lines 5-6 * * page 10, lines 4-9 * * page 14, line 1 - page 15, line 9 * -----	1-15	INV. C11D1/06 C11D3/00 C11D3/386
X	US 2007/111914 A1 (HSU FENG-LUNG G [US] ET AL) 17 May 2007 (2007-05-17) * page 1, paragraphs 0003,0016 * * page 1, paragraph 0018 - page 2, paragraph 0020 * * page 2, paragraphs 0024,0036-0037 * * page 5, paragraph 0077 * * page 6, paragraph 0084-0088 * * page 8, paragraph 0119 - page 9; examples 1-5; tables 1-4 * * claims 1,2,5,6 * * abstract * -----	14,15	TECHNICAL FIELDS SEARCHED (IPC) C11D
X	WO 2019/092191 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC D/B/A UNILEVER [US]) 16 May 2019 (2019-05-16) * claims 1-4 * * page 1, lines 15-19 * * page 3, lines 9-21 * * page 5, lines 4-7 * * page 8, line 5 - page 12, line 18 * -----	14,15 1-13	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 12 November 2019	Examiner Gault, Nathalie
CATEGORY OF CITED DOCUMENTS 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	

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 19 17 9593

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016198263 A1	15-12-2016	CL 2017003036 A1	11-05-2018
		CN 107735487 A	23-02-2018
		EP 3307862 A1	18-04-2018
		PH 12017502036 A1	11-04-2018
		TR 201906929 T4	21-05-2019
		US 2018155657 A1	07-06-2018
		WO 2016198263 A1	15-12-2016
		ZA 201707292 B	27-02-2019

US 2007111914 A1	17-05-2007	AU 2006314866 A1	24-05-2007
		BR PI0618660 A2	06-09-2011
		CA 2625950 A1	24-05-2007
		EP 1948768 A1	30-07-2008
		US 2007111914 A1	17-05-2007
		WO 2007057085 A1	24-05-2007
		ZA 200803705 B	28-10-2009

WO 2019092191 A1	16-05-2019	NONE	

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- WO 2017055205 A1 [0009]
- WO 2016180552 A1 [0010]
- EP 218272 A [0043]
- EP 331376 A [0043]
- GB 1372034 A [0043]
- WO 9506720 A [0043]
- WO 9627002 A [0043]
- WO 9612012 A [0043]
- JP 64744992 B [0043]
- WO 9116422 A [0043]
- WO 0060063 A [0044] [0048]
- WO 9942566 A [0044]
- WO 02062973 A [0044] [0048]
- WO 9704078 A [0044]
- WO 9704079 A [0044]
- US 5869438 A [0044]
- WO 2004101759 A [0048]
- WO 2004101760 A [0048]
- WO 2004101763 A [0048]
- US 6939702 B1 [0048]
- WO 2007087243 A [0049]
- EP 0384070 A [0066]
- EP 266863 A [0072]
- WO 9219709 A [0095]
- WO 9219708 A [0095]
- WO 2005003274 A [0101]
- WO 2006032327 A [0101]
- WO 2006032397 A [0101]
- WO 2006045275 A [0101]
- WO 06027086 A [0101]
- WO 2008017570 A [0101]
- WO 2008141880 A [0101]
- WO 2009132870 A [0101]
- WO 2009141173 A [0101]
- WO 2010099997 A [0101]
- WO 2010102861 A [0101]
- WO 2010148624 A [0101]
- WO 2008087497 A [0101] [0102]
- WO 2011011799 A [0101]
- WO 2012054820 A [0101]
- WO 2013142495 A [0101] [0102]
- WO 2013151970 A [0101]
- WO 2012054058 A [0103]
- WO 2010151906 A [0103]

Non-patent literature cited in the description

- Enzymes in Detergency. Marcel Dekker, 1997 [0042]
- **DARTOIS et al.** *Biochemica et Biophysica Acta*, 1993, vol. 1131, 253-360 [0043]
- **POUCHER.** *Journal of the Society of Cosmetic Chemists*, 1955, vol. 6 (2), 80 [0077]
- **FENAROLI'S.** Handbook of Flavor Ingredients. CRC Press, 1975 [0080]
- **M. B. JACOBS.** Synthetic Food Adjuncts. 1947 [0080]
- **S. ARCTANDER.** *Perfume and Flavor Chemicals*, 1969 [0080]
- **H ZOLLINGER.** Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments. Wiley VCH, 2003 [0097]
- Industrial Dyes Chemistry, Properties Applications. Wiley-VCH, 2003 [0097]
- *CHEMICAL ABSTRACTS*, 72749-80-5 [0105]