



(51) International Patent Classification:

C11D 1/06 (2006.01) C11D 3/00 (2006.01)
C11D 1/37 (2006.01)

(21) International Application Number:

PCT/EP2019/059128

(22) International Filing Date:

10 April 2019 (10.04.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

18172957.5 17 May 2018 (17.05.2018) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,

CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available):

ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: CLEANING COMPOSITION COMPRISING RHAMNOLIPID AND ALKYL ETHER CARBOXYLATE SURFACTANTS

(57) Abstract: The invention relates to a cleaning composition comprising: a) from 1 to 20 wt.% of a rhamnolipid anionic surfactant; and b) from 0.1 to 20 wt.% of an alkyl ether carboxylic acid surfactant of the following structure: $R_2-(OCH_2CH_2)_n-OCH_2-COOH$, wherein: R_2 is selected from saturated and mono-unsaturated C10 to C20 linear or branched alkyl chains, preferably selected from: C₁₂; C₁₄; C₁₆; and, C₁₈ linear alkyl chains, wherein n is selected from 5 to 30, preferably from 10 to 20, and wherein the weight fraction of alkyl ether carboxylic acid to rhamnolipid surfactant is from 0.05 to 10, preferably from 0.1 to 3; and to a domestic method of treating a textile with an aqueous solution of said cleaning composition.



CLEANING COMPOSITION COMPRISING RHAMNOLIPID AND ALKYL ETHER CARBOXYLATE SURFACTANTS

Field of Invention

The invention concerns a cleaning composition comprising a rhamnolipid surfactant and an
5 alkyl ether carboxylic acid surfactant.

Background of the Invention

Rhamnolipids are carboxylic acid containing anionic surfactants that consists of one or more
alkyl chains connected via a beta hydroxy group to a rhamnose sugar. They may be
10 produced by various bacterial species. When used as detergent actives in cleaning
compositions, in particular laundry cleaning compositions, large quantities of foam is created
which is difficult to remove.

These is a need for effective cleaning compositions containing rhamnolipids with reduced
15 foaming.

Summary of the Invention

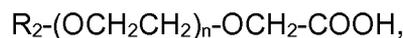
We have found that cleaning compositions containing a rhamnolipid surfactant and a specific
alkyl ether carboxylic acid surfactant give reduced levels of foaming.

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The invention relates in a first aspect to a cleaning composition comprising:

- a) from 1 to 20 wt.% of a rhamnolipid anionic surfactant; and
- b) from 0.1 to 20 wt.% of an alkyl ether carboxylic acid surfactant of the following
structure:

25



wherein:

R_2 is selected from saturated and mono-unsaturated C_{10} to C_{20} linear or
branched alkyl chains, preferably selected from: C_{12} ; C_{14} ; C_{16} ; and, C_{18} linear
30 alkyl chains, wherein n is selected from 5 to 30, preferably from 10 to 20, and
wherein the weight fraction of alkyl ether carboxylic acid to rhamnolipid
surfactant is from 0.05 to 10, preferably from 0.1 to 3.

Preferably the cleaning composition is a fluid cleaning composition, more preferably an aqueous cleaning composition.

5 Preferably the cleaning composition comprises from 0 to 20 wt.%, more preferably from 0 to 10 wt.% of additional surfactants, wherein if present, the weight fraction of additional surfactant to the sum of (rhamnolipid plus alkyl ether carboxylate/carboxylic acid surfactant) is from 0 to 1.

10 Preferably the composition comprises at most of 1 wt.% of phosphorous containing chemicals, more preferably the composition comprises from 0 to 1 wt.% of phosphorous containing chemicals.

15 Preferably the composition comprises from 0.5 to 6 wt.%, more preferably from 1 to 6 wt.%, most preferably from 2 to 6 wt.% of the alkyl ether carboxylic acid anionic surfactant.

Preferably the alkyl chain, the R₂ group, of the alkyl ether carboxylic acid anionic surfactant is selected from saturated and mono-unsaturated C₁₆ to C₁₈ linear alkyl chains.

20 Preferably the rhamnolipid is present in the composition at a level of from 1.5 to 15 wt.%, more preferably from 2 to 8 wt.%.

Preferably, the rhamnolipid comprises at least 50 wt.% di-rhamnolipid, more preferably at least 60 wt.% di-rhamnolipid, even more preferably 70 wt.% di-rhamnolipid, most preferably at least 80 wt.% di-rhamnolipid.

25 Preferably the rhamnolipid is a di-rhamnolipid of formula: Rha₂C₈₋₁₂C₈₋₁₂. The preferred alkyl chain length is from C₈ to C₁₂, the alkyl chain may be saturated or unsaturated.

30 Preferably the composition is a home care cleaning composition and further comprises one or more enzymes selected from lipases, proteases, amylases, cellulases, and mixtures thereof.

Preferably the cleaning composition is a laundry detergent composition, more preferably a liquid laundry detergent or a powder detergent. Preferably when a liquid detergent, the

laundry detergent composition when dissolved in demineralised water at 4g/L, 293K, has a pH of from 6 to 11, more preferably from 7 to 9.

The invention further relates in a second aspect to a domestic method of treating a textile, the method comprising the steps of:

- a) treating a textile with from 1 g/L of an aqueous solution of the cleaning composition as defined in the first aspect; and,
- b) allowing said aqueous solution to remain in contact with the textile for a time period of from 10 minutes to 2 days, then rinsing and drying the textile.

It is intended that any preferable subject matter described herein can be combined with any other subject matter, particularly combining 2 or more preferable subject matters.

Detailed Description of the Invention

Alkyl Ether Carboxylic Acid

The cleaning composition comprises from 0.1 to 20 wt.%, preferably from 0.5 to 6 wt.%, more preferably from 1 to 6 wt.%, most preferably from 2 to 6 wt.% of the alkyl ether carboxylic acid anionic surfactant.

Weights of alkyl ether carboxylic acid are calculated as the protonated form, $R_2-(OCH_2CH_2)_n-OCH_2COOH$. The alkyl ether anionic surfactant may be in carboxylic acid form, or it may be in alkyl ether carboxylate surfactant form. The alkyl ether carboxylate/carboxylic acid anionic surfactant may be used as salt version, for example with a counterion such as a sodium salt, or an amine salt.

The alkyl chain may be linear or branched, preferably it is linear.

The alkyl chain may be aliphatic or contain one cis or trans double bond.

The alkyl chain (R_2) is selected from saturated and mono-unsaturated C_{10} to C_{20} linear or branched alkyl chains preferably selected from: C_{12} ; C_{14} ; C_{16} ; and, C_{18} linear alkyl chain. The alkyl chain is preferably selected from $CH_3(CH_2)_{11}$, $CH_3(CH_2)_{13}$, $CH_3(CH_2)_{15}$, $CH_3(CH_2)_{17}$, $CH_3(CH_2)_7CH=CH(CH_2)_8$ -. It is preferred that the R_2 is selected from C_{16} to C_{18} linear alkyl chains. Most preferably the alkyl chain is $CH_3(CH_2)_7CH=CH(CH_2)_8$ -.

The alkyl ether carboxylic acid has n selected from 5 to 30, preferably from 10 to 20.

The weight fraction of alkyl ether carboxylic acid to rhamnolipid surfactant is from 0.05 to 10, preferably from 0.1 to 3.

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Alkyl ether carboxylic acid are available from Kao (Akypo®), Huntsman (Empicol®) and Clariant (Emulsogen®).

Alkyl ether carboxylic acids synthesis is discussed in Anionic Surfactants Organic Chemistry edited by H.W. Stache (Marcel Dekker, New York 1996).

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They may be synthesised via the reaction of the corresponding alcohol ethoxylate with chloroacetic acid or monochloro sodium acetate in the presence of NaOH:-



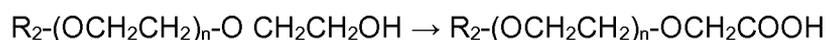
In this synthesis residual $R_2-(OCH_2CH_2)_n-OH$ may be present, preferably levels of $R_2-(OCH_2CH_2)_n-OH$ are from 0 to 10 wt.% in the alkyl ether carboxylic acid. Low levels of diglycolic acid and glycolic acid may be present as bi products.

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NaCl from the synthesis may be present in the aqueous liquid laundry detergent composition. Additional NaCl may be added to the composition.

They alkyl ether carboxylic acid may also be synthesised via an oxidation reaction:-

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The oxidation is typically conducted using oxygen as the oxidant under basic conditions in the presence of metal catalyst such as Pd/Pt, as described in DE3135946; DE2816127 and EP0304763.

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Rhamnolipids

Rhamnolipids are a class of glycolipid. They are constructed of rhamnose combined with beta-hydroxy fatty acids. Rhamnose is a sugar. Fatty acids are ubiquitous in animals and plants.

35

Rhamnolipids are discussed in Applied Microbiology and Biotechnology (2010) 86:1323-1336 by E. Deziel *et al.* Rhamnolipids are produced by Glycosurf, AGAE Technologies and Urumqi Unite Bio-Technology Co., Ltd. Rhamnolipids may be produced by strains of the bacteria *Pseudomonas Aeruginosa*. Rhamnolipids may also be produced by a recombinant cell of *Pseudomonas Putida* where the recombinant cell comprises increased activity of at least one of the enzymes a/P hydrolase, rhamnosyltransferase I or rhamnosyl-transferase II compared to the wild-type of the cell.

There are two major groups of rhamnolipids; mono-rhamnolipids and di-rhamnolipids.

Mono-rhamnolipids have a single rhamnose sugar ring. A typical mono-rhamnolipid produced by *P. aeruginosa* is L-rhamnosyl- β -hydroxydecanoyl- β -hydroxydecanoate (RhaC₁₀C₁₀). It may be referred to as Rha-C₁₀-C₁₀, with a formula of C₂₆H₄₈O₉. Mono-rhamnolipids have a single rhamnose sugar ring.

The IUPAC Name is 3-[3-[(2R,3R,4R,5R,6S)-3,4,5-trihydroxy-6-methyloxan-2-yl]oxydecanoyloxy]decanoic acid.

Di-rhamnolipids have two rhamnose sugar rings. A typical di-rhamnolipid is L-rhamnosyl-L-rhamnosyl- β -hydroxydecanoyl- β -hydroxydecanoate (Rha₂C₁₀C₁₀). It may be referred to as Rha-Rha-C₁₀-C₁₀, with a formula of C₃₂H₅₈O₁₃.

The IUPAC name is 3-[3-[4,5-dihydroxy-6-methyl-3-(3,4, 5-tri hydroxy-6-m ethyloxan-2-yl)oxyoxan-2-yl]oxydecanoyloxy]decanoic acid.

In practice a variety of other minor components with different alkyl chain length combinations, depending upon carbon source and bacterial strain, exist in combination with the above more common rhamnolipids. The ratio of mono-rhamnolipid and di-rhamnolipid may be controlled by the production method. Some bacteria only produce mono-rhamnolipid, see US5767090: Example 1, some enzymes can convert mono-rhamnolipid to di-rhamnolipid.

In various publications mono-rhamnolipids have the notation Rha-, which may be abbreviated as Rh or RL2. Similarly, di-rhamnolipids have the notation Rha-Rha or Rh-Rh- or RL1. For historical reasons "rhamnolipid 2" is a mono-rhamnolipid and "rhamnolipid 1" is

a di-rhamnolipid. This leads to some ambiguity in the usage of "RL1 " and "RL2" in the literature.

Throughout this patent specification, we use the terms mono- and di-rhamnolipid in order to avoid this possible confusion. However, if abbreviations are used R1 is mono-rhamnolipid and R2 is di-rhamnolipid. For more information on the confusion of terminology in the prior art see the introduction to US 4814272.

The following rhamnolipids have been detected as produced by the following bacteria:
 10 (C12:1, C14:1 indicates fatty acyl chains with double bonds).

Rhamnolipids produced by *P. aeruginosa* (mono-rhamnolipids):

Rha-C8-C10, Rha-C10-C8, Rha-C-10-C10, Rha-C10-C12, Rha-C10-C12: 1 , Rha-C12-C10, Rha-C12: 1-C10

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Rhamnolipids produced by *P. aeruginosa* (di-rhamnolipids):

Rha-Rha-C8-C10, Rha-Rha-C8-C12: 1 , Rha-Rha-C10-C8, Rha-Rha-C10-C10, Rha-Rha-C10-C12: 1 , Rha- Rha-C-10-C-12, Rha-Rha-C-12-C-10, Rha-Rha-C-12: 1-C-12, Rha-Rha-C-10- C14: 1

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Rhamnolipids produced by *P. aeruginosa* (unidentified as either mono- or di-rhamnolipids):

C8-C8, C8-C10, C10-C8, C8-C12: 1 , C12: 1-C8, C10-C10, C12-C10, C12: 1-C10 C12-C12, C12: 1-C12, C14-C10, C14: 1-C10, C14-C14.

25 Rhamnolipids produced by *P. chlororaphis* (mono-rhamnolipids only):

Rha-C10-C8, Rha-C10 -C10, Rha-C12-C10, Rha-C12: 1-C10, Rha-C12-C12, Rha-C12: 1-C12, Rha-C14-C10. Rha-C-14; 1- C-10.

Rhamnolipids produced by *Burkholderia pseudomallei* (di-rhamnolipids only):

30 Rha-Rha-C14-C14.

Rhamnolipids produced by *Burkholderia (Pseudomonas) plantarii* (di-rhamnolipids only):

Rha-Rha-C14-C14.

There are over 100 strains of *P. aeruginosa* on file at the American Type Culture Collection (ATCC). There are also a number of strains that are only available to manufacturers of commercial Rhamnolipids. Additionally there are probably thousands of strains isolated by various research institutions around the world. Some work has gone into typing them into groups. Each strain has different characteristics including how much rhamnolipid is produced, which types of rhamnolipids are produced, what it metabolizes, and conditions in which it grows. Only a small percentage of the strains have been extensively studied.

Through evaluation and selection, strains of *P. aeruginosa* can be isolated to produce rhamnolipids at higher concentrations and more efficiently. Strains can also be selected to produce less byproduct and to metabolize different feedstock or pollutants. This production is greatly affected by the environment in which the bacterium is grown.

A typical di-rhamnolipid is L-rhamnosyl-L-rhamnosyl- β -hydroxydecanoyl- β -hydroxydecanoate (Rha₂C₁₀C₁₀ with a formula of C₃₂H₅₈O₁₃).

In practice a variety of other minor components with different alkyl chain length combinations, depending upon carbon source and bacterial strain, exist in combination with the above more common rhamnolipids. The ratio of mono-rhamnolipid and di-rhamnolipid may be controlled by the production method. Some bacteria only produce mono-rhamnolipid, see US5767090: Example 1, some enzymes can convert mono-rhamnolipid to di-rhamnolipid.

Preferably the rhamnolipid is present in the formulation from 1.5 to 15 wt.%, more preferably from 2 to 8 wt.%.

Preferably the rhamnolipid is selected from:

- Rhamnolipids produced by *P. aeruginosa* (mono-rhamnolipids):

Rha-C8-C10, Rha-C10-C8, Rha-C10-C10, Rha-C10-C12, Rha-C10-C12:1, Rha-C12-C10, Rha-C12:1-C10

- Rhamnolipids produced by *P. chlororaphis* (mono-rhamnolipids only):

Rha-C10-C8, Rha-C10-C10, Rha-C12-C10, Rha-C12:1-C10, Rha-C12-C12, Rha-C12:1-C12, Rha-C14-C10, Rha-C14:1-C10.

- Mono-rhamnolipids may also be produced from *P. putida* by introduction of genes *rhlA* and *rhlB* from *Pseudomonas aeruginosa* [Cha et al. in *Bioresour Technol.* 2008. 99(7):2192-9]
- Rhamnolipids produced by *P. aeruginosa* (di-rhamnolipids):
 - 5 Rha-Rha-C8-C10, Rha-Rha-C8-C12:1, Rha-Rha-C10-C8, Rha-Rha-C10-C10, Rha-Rha-C10-C12:1, Rha-Rha-C10-C12, Rha-Rha-C12-C10, Rha-Rha-C12:1-C12, Rha-Rha-C10-C14:1
- Rhamnolipids produced by *Burkholderia pseudomallei* (di-rhamnolipids only):
Rha-Rha-C14-C14.
- 10 - Rhamnolipids produced by *Burkholderia* (*Pseudomonas*) *plantarii* (di-rhamnolipids only):
Rha-Rha-C14-C14.
- Rhamnolipids produced by *P. aeruginosa* which are initially unidentified as either mono- or di-rhamnolipids:
 - 15 C8-C8, C8-C10, C10-C8, C8-C12:1, C12:1-C8, C10-C10, C12-C10, C12:1-C10, C12-C12, C12:1-C12, C14-C10, C14:1-C10, C14-C14.

Preferably the Rhamnolipid is L-rhamnosyl- β -hydroxydecanoyl- β -hydroxydecanoate (RhaC₁₀C₁₀ with a formula of C₂₆H₄₈O₉).

20

Preferably, the rhamnolipid comprises at least 50 wt.% di-rhamnolipid, more preferably at least 60 wt.% di-rhamnolipid, even more preferably 70 wt.% di-rhamnolipid, most preferably at least 80 wt.% di-rhamnolipid.

25 Preferably the rhamnolipid is a di-rhamnolipid of formula: Rha₂C₈₋₁₂C₈₋₁₂. The preferred alkyl chain length is from C₈ to C₁₂. The alkyl chain may be saturated or unsaturated.

Cleaning Composition

The composition is a cleaning composition, useful for cleaning a substrate, for example a surface, including for home and personal care purposes. The composition is preferably a fluid cleaning composition, more preferably an aqueous cleaning composition.

35 Preferably the cleaning composition is a home care composition. Preferably the cleaning composition is a laundry detergent composition, more preferably a liquid laundry detergent or a powder detergent.

Preferably when a liquid detergent, the laundry detergent composition when dissolved in demineralised water at 4g/L, 293K, has a pH of from 6 to 11, more preferably from 7 to 9.

5 Additional Surfactants

Additional surfactants may be present in the composition.

Preferably the cleaning composition comprises from 0 to 20 wt.%, more preferably from 0 to 10 wt.% of additional surfactants, wherein if present, the weight fraction of additional surfactant to the sum of (rhamnolipid plus alkyl ether carboxylate/carboxylic acid surfactant) is from 0 to 1.

These are preferably selected from anionic and nonionic surfactants.

15 In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn, Carl Hauser Verlag, 1981. Preferably the surfactants used are saturated.

Preferred nonionic detergent compounds which may be used include the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are the condensation products of aliphatic primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO, preferably 7EO to 9EO.

Preferred 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 acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₁₀ to C₂₀ benzene sulphates, particularly sodium linear secondary alkyl C₁₀ to C₁₅ benzene sulphates; 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. The preferred anionic detergent compounds are sodium C₁₁ to C₁₅ alkyl benzene sulphonates and sodium C₁₂ to C₁₄ alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular, the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C₁₂ to C₁₄ primary alcohol sulphate together with a C₁₂ to C₁₆ primary alcohol 3 to 7 EO ethoxylate.

Preferably the additional surfactant is predominately anionic surfactant by weight.

15

Further Ingredients

The composition may comprise any of these further preferred ingredients.

Builders or Complexing Agents

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

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Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

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.

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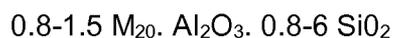
The composition may also contain 0-65 % of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue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

5

Zeolite and carbonate (including bicarbonate and sesquicarbonate) are preferred builders.

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 15 wt.%. Aluminosilicates are materials having the general formula:

10



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.

15

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. The ratio of surfactants to aluminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

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Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term 'phosphate' embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

25

Preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt.% of phosphate. Preferably the laundry detergent formulation is carbonate built if a builder is included.

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Fluorescent Agent

The composition preferably comprises 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

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or agents used in the composition is generally from 0.005 to 2 wt.%, more preferably 0.01 to 0.1 wt.%. 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.

It is preferred that the aqueous solution used in the method has a fluorescer present. When a fluorescer is present in the aqueous solution used in the method it is preferably in the range from 0.0001 g/l to 0.1 g/l, preferably 0.001 to 0.02 g/l.

Dye

The composition preferably comprises a dye. Dyes are discussed in K.Hunger (ed). Industrial Dyes: Chemistry, Properties, Applications (Weinheim: Wiley-VCH 2003). Organic dyes are listed in the colour index (Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists)

Preferred dye chromophores are azo, azine, anthraquinone, phthalocyanine and triphenylmethane.

Azo, anthraquinone, phthalocyanine and triphenylmethane dyes preferably carry a net anionic charged or are uncharged. Azine dyes preferably carry a net anionic or cationic charge.

Preferred non-shading dyes are selected from blue dyes, most preferably anthraquinone dyes bearing sulphonate groups and triphenylmethane dye bearing sulphonate groups. Preferred compounds are acid blue 80, acid blue 1, acid blue 3; acid blue 5, acid blue 7, acid blue 9, acid blue 11, acid blue 13, acid blue 15, acid blue 17, acid blue 24, acid blue 34, acid blue 38, acid blue 75, acid blue 83, acid blue 91, acid blue 97, acid blue 93, acid blue 93:1, acid blue 97, acid blue 100, acid blue 103, acid blue 104, acid blue 108, acid blue 109, acid blue 110, and acid blue 213. On dissolution granules with non-shading dyes provide an attractive colour to the wash liquor.

Blue or violet Shading dyes are most preferred. 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 260 to 320, most preferably 270 to 300. The white cloth used in this test is
5 bleached non-mercerised woven cotton sheeting.

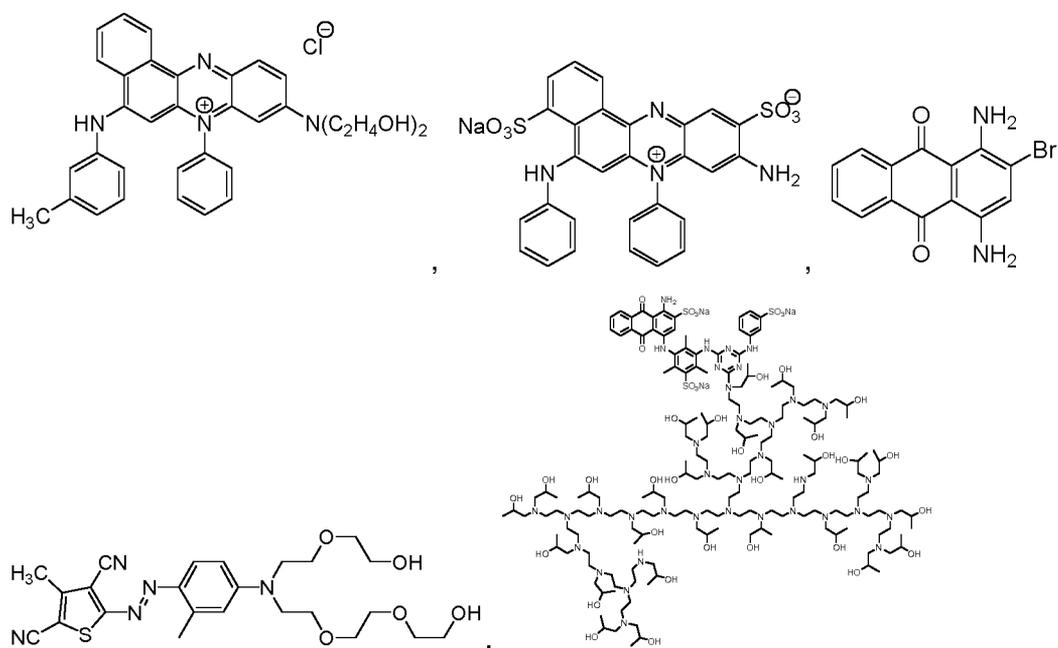
Shading dyes are discussed in WO 2005/003274, WO 2006/032327(Unilever), WO 2006/032397(Unilever), WO 2006/045275(Unilever), WO 2006/027086(Unilever), WO 2008/017570(Unilever), WO 2008/141880(Unilever), WO 2009/132870(Unilever), WO
10 2009/141 173 (Unilever), WO 2010/099997(Unilever), WO 2010/102861 (Unilever), WO 2010/148624(Unilever), WO 2008/087497 (P&G), WO 2011/011799 (P&G), WO 2012/054820 (P&G), WO 2013/142495 (P&G) and WO 2013/151970 (P&G).

A mixture of shading dyes may be used.
15

The shading dye chromophore is most preferably selected from mono-azo, bis-azo, anthraquinone, and azine.

Mono-azo dyes preferably contain a heterocyclic ring and are most preferably thiophene
20 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.

Most preferred shading dyes are selected from Direct Violet 9, Direct Violet 99, Direct Violet
25 35, Solvent Violet 13, Disperse Violet 28, dyes of the structure



Perfume

- 5 Preferably the composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt.%, most preferably 0.1 to 1 wt.%. 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.

10

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.

15

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.

20

It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

Polymers

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

5 copolymers. Polymers present to prevent dye deposition, for example poly(vinylpyrrolidone), poly(vinylpyridine-N-oxide), and poly(vinylimidazole), may be present in the formulation.

Enzymes

One or more enzymes are preferred to be present in a cleaning composition of the invention
10 and when practicing a method of the invention.

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

15 Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from Humicola
20 (synonym Thermomyces), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, 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* (WO 96/12012), a *Bacillus* lipase, e.g. from
25 *B. subtilis* (Dartois et al. (1993), *Biochemica et Biophysica Acta*, 1 131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

Other examples are lipase variants such as those described in WO 92/05249, WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292, WO 95/30744, WO 94/25578, WO
30 95/14783, WO 95/22615, WO 97/04079 and WO 97/07202, WO 00/60063.

Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ and lipoclean™ (Novozymes A/S).

The method of the invention may be carried out in the presence of phospholipase classified as EC 3.1.1 .4 and/or EC 3.1.1 .32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids.

5 Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A₁ and A₂
10 which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid.

Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or
15 phosphatidic acid respectively.

The enzyme and the photobleach may show some interaction and should be chosen such that this interaction is not negative. Some negative interactions may be avoided by encapsulation of one or other of enzyme or photobleach and/or other segregation within the
20 product.

Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or
25 a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

30 The method of the invention may be carried out in the presence of cutinase classified in EC 3.1.1 .74. The cutinase used according to the invention may be of any origin.

Preferably cutinases are of microbial origin, in particular, of bacterial, of fungal or of yeast origin.

35

Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin.

Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus*, e.g. a special strain of *B. licheniformis*,
5 described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

10 Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g. the fungal cellulases produced from *Humicola insolens*, *Thielavia terrestris*, *Myceliophthora thermophila*, and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691
15 ,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307.

Commercially available cellulases include Celluzyme™, Carezyme™, Celluclean™,

Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor
20 International Inc.), and KAC-500(B)™ (Kao Corporation).

Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin.

Chemically modified or protein engineered mutants are included. Examples of useful
25 peroxidases include peroxidases from *Coprinus*, e.g. from *C. cinereus*, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257.

Commercially available peroxidases include Guardzyme™ and Novozym™ 51004
(Novozymes A/S).

30

Further enzymes suitable for use are discussed in WO 2009/087524, WO 2009/090576, WO 2009/107091, WO 2009/111258 and WO 2009/148983.

Enzyme Stabilizers

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.

Where alkyl groups are sufficiently long to form branched or cyclic chains, the alkyl groups encompass branched, cyclic and linear alkyl chains. The alkyl groups are preferably linear or branched, most preferably linear.

The indefinite article "a" or "an" and its corresponding definite article "the" as used herein means at least one, or one or more, unless specified otherwise.

The invention will be further described with the following non-limiting examples.

Examples

Example 1

Rhamnolipid (RL-A) from *Pseudomonas aeruginosa* (CAS-No 869062-42-0) was purchased from Aldrich and used as supplied. Aldrich obtained the rhamnolipid from AGAE technology. The rhamnolipid product is a mixture of monorhamnolipids and dirhamnolipids with (Rha-Rha-C₁₀-C₁₀ and Rha-C₁₀-C₁₀) as predominant. The alkyl ether carboxylate was Emulsogen COL100 supplied by Clariant, it is oleyl based with 10 moles of ethoxylation.

An aqueous liquid laundry detergent formulation was created containing 6 wt.% of Rhamnolipid (RL-A). This was added to 26 French hard water to give an aqueous solution containing 4g/L of Rhamnolipid (RL1). 25g of the solution was decanted in to a 125ml glass bottle without the creation of any foam. A lid was placed on the bottle and it was carefully placed on its axis on an orbital shaker and rotated at 200 rpm for 30 seconds. The bottle was removed and stood on a flat surface and the foam height measured, as the distance from the top of the liquid to the top of the foam. The experiment was repeated but using 6 wt.% Alkyl Ether Carboxylate (AEC). All experiments were repeated eight times and these reference results shown in the table below.

	Foam height in cm	95% confidence
RL-A	36.125	1.868
AEC	17.250	1.095

From these results a mixture of AEC and RL-A would be expected to have a foam height of:

$$\text{Foam height} = 36.125 - 0.1888 * (\% \text{AEC})$$

5

Where %AEC is the percent of AEC in the mixture.

The experiment was repeated with mixtures of AEC and RL-A and the experimental and expected foam heights given in the table below. These experiments were performed in quadruplet.

10

%RL-A	%AEC	Expected foam height	Measured foam height	95% confidence
90	10	34.2	26.0	1.6
50	50	26.7	19.3	0.9
25	75	22.0	15.8	0.9

The mixture of AEC and RL-A produces much lower levels of foam than expected from the individual components.

15

Example 2

The experiments were repeated with a different Rhamnolipid (RL-B) obtained from Evonik. (Lx P001). The rhamnolipid is predominately a di-rhamnolipid of formula: $\text{Rha}_2\text{C}_{8-12}\text{C}_{8-12}$. The neat rhamnolipid gave the following foam (5 repeats):

20

	Foam height in cm	95% confidence
RL-B	43.6	2.4

From this result and the AEC result of example 1, a mixture of AEC and RL would be expected to have a foam height of:

25

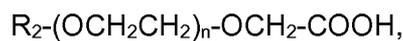
$$\text{Foam height} = 43.6 - 0.2635 * (\% \text{AEC})$$

When in a 50:50 mixture with Emulsogen COL100, much lower levels of foam than expected from the individual components was obtained (5 repeats):

%RL-B	%AEC	Expected foam height	Measured foam height	95% confidence
50	50	30.4	24.4	2.5

CLAIMS

1. A cleaning composition comprising:
- a) from 1 to 20 wt.% of a rhamnolipid anionic surfactant; and
- 5 b) from 0.1 to 20 wt.% of an alkyl ether carboxylic acid surfactant of the following structure:



wherein:

10 R_2 is selected from saturated and mono-unsaturated C_{10} to C_{20} linear or branched alkyl chains, preferably selected from: C_{12} ; C_{14} ; C_{16} ; and, C_{18} linear alkyl chains, wherein n is selected from 5 to 30, preferably from 10 to 20, and wherein the weight fraction of alkyl ether carboxylic acid to rhamnolipid surfactant is from 0.05 to 10, preferably from 0.1 to 3.

15

2. A composition according to claim 1, wherein the cleaning composition is a laundry detergent composition, preferably a liquid laundry detergent or a powder detergent.
3. A composition according to claim 1 or claim 2, wherein the cleaning composition is a
- 20 fluid cleaning composition, more preferably an aqueous cleaning composition.
4. A composition according to any preceding claim, wherein the cleaning composition comprises from 0 to 20 wt.%, more preferably from 0 to 10 wt.% of additional surfactants, wherein if present, the weight fraction of additional surfactant to the sum of
- 25 (rhamnolipid plus alkyl ether carboxylate/carboxylic acid surfactant) is from 0 to 1.
5. A composition according to any preceding claim, wherein the composition comprises at most of 1 wt.% of phosphorous containing chemicals, for example the composition comprises from 0 to 1 wt.% of phosphorous containing chemicals.
- 30
6. A composition according to any preceding claim, wherein the composition comprises from 0.5 to 6 wt.%, more preferably from 1 to 6 wt.%, most preferably from 2 to 6 wt.% of the alkyl ether carboxylic acid anionic surfactant.

7. A composition according to any preceding claim, wherein the alkyl chain, the R₂ group, of the alkyl ether carboxylic acid anionic surfactant is selected from saturated and mono-unsaturated C₁₆ to C₁₈ linear alkyl chains.
- 5 8. A composition according to any preceding claim, wherein the rhamnolipid is present in the composition at a level of from 1.5 to 15 wt.%, more preferably from 2 to 8 wt.%.
9. A composition according to any preceding claim, wherein the rhamnolipid comprises at least 50 wt.% di-rhamnolipid, more preferably at least 60 wt.% di-rhamnolipid, even
10 more preferably 70 wt.% di-rhamnolipid, most preferably at least 80 wt.% di-rhamnolipid.
10. A composition according to any preceding claim, wherein the rhamnolipid is a di-rhamnolipid of formula: Rha₂C₈₋₁₂C₈₋₁₂.
- 15 11. A composition according to any preceding claim, wherein the composition is a home care cleaning composition and further comprises one or more enzymes selected from lipases, proteases, amylases, cellulases, and mixtures thereof.
- 20 12. A composition according to any preceding claim, wherein when a liquid laundry detergent, the laundry detergent composition when dissolved in demineralised water at 4g/L, 293K has a pH of from 6 to 11, more preferably from 7 to 9.
13. A domestic method of treating a textile, the method comprising the steps of:
25 a) treating a textile with from 1 g/L of an aqueous solution of the cleaning composition as defined in any one of claims 1 to 12; and,
b) allowing said aqueous solution to remain in contact with the textile for a time period of from 10 minutes to 2 days, then rinsing and drying the textile.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/059128

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C11D1/06 C11D1/37 C11D3/00
 ADD.

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

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C11D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 196 48 439 A1 (HENKEL KGAA [DE]) 28 May 1998 (1998-05-28) table 1; compounds A1,B1,B3,B4 -----	1-13
A	US 2014/296125 A1 (KUPPERT DIRK [DE] ET AL) 2 October 2014 (2014-10-02) example 5 -----	1-13

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 29 May 2019	Date of mailing of the international search report 18/06/2019
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Culmann, J
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/059128

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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