(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 April 2024 (11.04.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/074247 A1

(51) International Patent Classification:
*C11D 1/22* (2006.01) *C11D 3/50* (2006.01)
*C11D 1/24* (2006.01) *C11D 17/04* (2006.01)

(21) International Application Number:
PCT/EP2023/073163

(22) International Filing Date:
23 August 2023 (23.08.2023)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
22200099.4 06 October 2022 (06.10.2022) EP

(71) Applicant *(for all designated States except AE, AG, AU, BB, BH, BN, BW, BZ, CA, CL, CR, CY, DE, DJ, DM, DO, EC, EG, GB, GD, GH, GM, GT, HN, IE, IL, IN, IQ, IR, IT, JM, JO, KE, KH, KN, KR, KW, LA, LC, LK, LS, MA, MD, MT, MU, MW, MY, MZ, NA, NG, NI, NZ, OM, PA, PE, PG, QA, RS, RU, RW, SA, SC, SD, SG, SL, SV, SZ, TH, TN, TR, TT, TZ, UG, US, VC, VN, WS, ZA, ZM, ZW)*: **UNILEVER IP HOLDINGS B.V.** [NL/NL]; Weena 455, 3013 AL Rotterdam (NL).

(71) Applicant *(for all designated States except AL, AO, AT, BA, BE, BF, BG, BJ, BR, CF, CG, CH, CI, CM, CN, CO, CU, CV, CZ, DK, DZ, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, JP, KM, KP, LR, LT, LU, LV, LY, MC, ME, MG, MK, ML, MN, MR, MX, NE, NL, NO, PH, PL, PT, RO, SE, SI, SK, SM, SN, ST, SY, TD, TG, UA, US, UZ)*: **UNILEVER GLOBAL IP LIMITED** [GB/GB]; Port Sunlight, Wirral Merseyside CH62 4ZD (GB).

(71) Applicant *(for US only)*: **CONOPCO, INC., D/B/A UNILEVER** [US/US]; 700 Sylvan Avenue, Englewood Cliffs, New Jersey 07632 (US).

(72) Inventors: **BATCHELOR, Stephen, Norman**; Unilever Innovation Centre Wageningen B.V. Bronland 14, 6708 WH Wageningen (NL). **RAJANARAYANA, Venkataraghavan**; Unilever Innovation Centre Wageningen B.V. Bronland 14, 6708 WH Wageningen (NL). **RAMESH, Apeksha**; Unilever Innovation Centre Wageningen B.V. Bronland 14, 6708 WH Wageningen (NL).

(74) Agent: **NEWBOULD, Frazer, Anthony**; Unilever Patent Group Bronland 14, 6708 WH Wageningen (NL).

(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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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, ME, 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))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

(54) Title: COMPOSITION

(57) Abstract: A detergent composition comprising linear alkyl benzene sulphonate (LAS) obtained from waste plastic feedstock, and a fragrance comprising a first perfume raw material (PRM1) selected from aldehydes and a second perfume raw material (PRM2) selected from linalool; verdox; limonene; citronellol; 3-cyclohexene-1-methanol, alpha, alpha, 4-trimethyl-, 1-acetate; tricyclo[4.2.1.1(2,5)]dec-3-en-9-ol acetate stereoisomer; and mixtures thereof, and wherein the LAS obtained from waste plastic feedstock comprises a benzene moiety obtained from waste plastic feedstock and an alkyl obtained from petroleum feedstock or plant-based feedstock.

WO 2024/074247 A1

# COMPOSITION

The present invention relates to improved laundry liquid compositions comprising linear alkyl benzene sulphonate.

WO 2017/027271 (P&G) discloses methods for producing detergent compounds from waste plastic feedstocks. More specifically, the invention relates to methods for producing detergent intermediates, including alkylbenzenes, paraffins, olefins, oxo alcohols, and surfactant derivatives thereof from waste plastic feedstock.

WO 2020/178597 (Oxford Sustainable Fuels Ltd) discloses a process for upgrading a pyrolysis oil derived from plastic or rubber.

Despite the prior art there remains a need for improved detergent formulations comprising linear alkyl benzene sulphonate (LAS).

The synthesis of the surfactant linear alkyl benzene sulphonate (LAS) is described in Anionic Surfactants: Organic Chemistry (Surfactant Science Series Vol 56 edited by H. Stache), Marcel Dekker 1995. The chemistry involves production of linear C10/13 olefins which are reacted with benzene to form linear alkyl benzene (LAB) and then sulphonated to give LAS. The olefins can be obtained from CO via *Fischer Tropsch* synthesis, but today are derived from petroleum.

The LAS produced is complex mix of compounds with varying chain length and isomers. The properties of LAS are determined by the composition of the mixture. This is particularly key when used in laundry liquid detergent, as small changes in structure can dramatically change the product viscosity and stability.

Modern society relies on plastic for a wide range of products, including the packaging of laundry liquid detergents. The recycling of plastic waste is a key issue. Many plastics cannot be recycled by mechanical means, an alternative is chemical recycling. In chemical recycling the plastic is pyrolysed to produce pyrolysis oil, a complex mixture of aromatics, alkanes, cycloalkanes, alkenes, cycloalkenes and oxygenates. Chemical recycling of plastic waste: Bitumen, solvents and polystyrene from pyrolysis oil in *Waste Management* 118 (2020) 139-147 by Baene-Gonzalez *et al* illustrates a typical product mix from pyrolysis oil. Agricutural and waste products, such as oils, plant shells and husks may also be used to make pyrolysis oil. Once produced pyrolysis oil may be

distilled to give the necessary raw materials to make LAS. The LAS so produced is not of the same specification as the petrochemical produced LAS due to the presence of minor components, that cannot be removed from the pyrolysis oil, such as low levels of other aromatics than benzene for example styrene and styrene derivatives. This difference means that pyrolysis produced LAS cannot be simply interchanged with petrochemical LAS due to the change in component make-up.

There is a need for a way to incorporate pyrolysis-based LAS into laundry detergent formulations without dramatically changing the detergent's properties. Preferably the amount of pyrolysis-based LAS is such that it compensates for the plastic packing used to transport the liquid detergent, by a factor of greater than 1, more preferably great than 10, most preferably greater than 100 times.

LAB is typically manufactured using petroleum feedstocks on a large scale by the petroleum industry. LAB is converted to LAS by smaller industrial plants before being incorporated as LAS acid in detergent compositions. In the composition the LAS acid is neutralised by a counterions with alkali metal salts or ammoniacal salts.

The key to LAS's success in detergent formulations is that it is a varied mixture of components. Variety resides in the number of carbon atoms in the alkyl chain as well as the point in the alkyl chain that the alkyl chain is linked to the benzene ring. There also exist isomers of LAS for example the 2-phenyl isomer which appears relevant to the overall performance of LAS in use.

The variety of materials present in a LAS batch also figures in the supply chain. The LAS, (or more correctly LAB) produced is influenced by the feedstock. Different petroleum feedstocks will produce different LAB mixtures. In the consumer products industry this is managed with reference to a specification which covers a range of LAB characteristics. The specification is designed to ensure that no matter the actual nature of any one sample, that it is able to function as required in a detergent formulation.

Functioning in a detergent formulation, in particular a liquid formulation is also important, not just for the detergency benefit provided by the LAS but the influence on the performance of other materials in the liquid laundry detergent composition.

Fragrances, surfactants, fluorescers and preservatives are heavily influenced by the nature of LAS and the specification is designed to ensure that these materials are not unduly affected by the varying nature of the LAS.

For this reason the incorporation of different feedstocks into the supply chain, while desirable, has huge consequences on the performance of LAS and also the other materials commonly found in laundry compositions.

We have surprisingly found that the use of waste plastic feedstocks in LAB production needs careful management before being able to provide a viable LAB raw material for detergent formulators.

Accordingly, and in a first aspect there is provided a detergent composition comprising linear alkyl benzene sulphonate (LAS) obtained from waste plastic feedstock, and a fragrance comprising a first perfume raw material (PRM1) selected from aldehydes and a second perfume raw material (PRM2) selected from linalool; verdox; limonene; citronellol; 3-cyclohexene-1-methanol, alpha, alpha, 4-trimethyl-, 1-acetate; tricyclo[4.2.1.1(2,5)]dec-3-en-9-ol acetate stereoisomer; and mixtures thereof, and wherein the LAS obtained from waste plastic feedstock comprises a benzene moiety obtained from waste plastic feedstock and an alkyl obtained from petroleum feedstock or plant-based feedstock.

We have surprisingly found that the performance of certain perfume raw materials is enhanced by the inclusion of LAS comprising a benzene moiety obtained from waste plastic feedstock instead of from petroleum. In particular, the perfume raw materials are more evident in the headspace when using LAS comprising a benzene moiety obtained from petroleum-based feedstock.

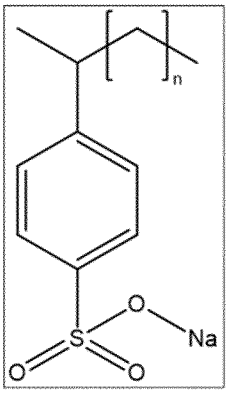
Further, the processing of the described levels of LAS obtained from waste plastic feedstock in the manufacture of laundry compositions comprising LAS is similarly not diminished whereas moving beyond these levels, a change in the processing or formulation is required.

Preferably, the detergent composition comprises from 1 to 40% LAS, more preferably from 2 to 10% wt. LAS.

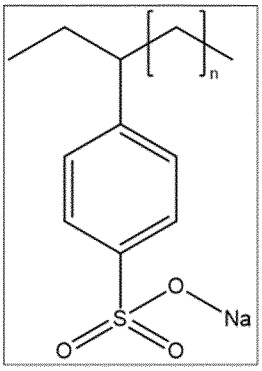
Preferably, the LAS obtained from waste plastic feedstock comprises alkyl chains with an average chain length from 8 to 14 carbons, more preferably from 10 to 13 and most preferably from 11 to 12.

Preferably, at least 30% wt. of the LAS obtained from waste plastic feedstock comprises alkyl chains with 12 carbons. Preferably, at least 30% wt. of the LAS obtained from waste plastic feedstock comprises alkyl chains with 11 carbons.

Preferably the waste-plastic feedstock derived LAS (pyrolysis LAS) is made via an alkylation reaction of benzene with an n-alkyl, then sulphonation. Preferably alkyl chains obtained from the pyrolysis oil and used to make the LAS have a distillation range of 174 to 220°C.




(A)




(B)

Preferably, the wt. ratio of (A):(B) is from 2:1 to 1:2, more preferably from 3:2 to 1:2, most preferably 5:4 to 4:5 in the pyrolysis LAS. Preferably these two isomers represent from 20 to 70wt% of the pyrolysis LAS, more preferably from 30 to40wt% .

During the addition reaction of the alkyl chain to the benzene ring in the production of LAS, non-benzene aromatics based side products may be produced, for example addition of the alkyl chain to styrene or addition of styrene to benzene. Toluene based products are another example. Preferably LAS adducts with non-benezene aromatics are less than 2wt% of the pyrolysis LAS. Preferably LAS adducts with styrene are less than 1wt% of the pyrolysis LAS.

Styrene monomers may be removed from pyrolysis oil by for example distillation or polymerisation and extraction.

In a preferred embodiment the benzene required for LAS synthesis is obtained from pyrolysis oil and the alkyl from plant sources. Olefiin can be obtained from plant oils by metathesis reactions as

described in Angewandte Chemie International Edition ; 51 (2012), 24. - S. 5802-5808 by Samir Chikkali and Stefan Mecking.

By petroleum derived LAS is meant LAS obtained directly from the petroleum supply chain and relates to the industry standard LAS. This therefore excludes LAS which is processed from waste-plastic which is involves extracting material from waste products, processing them to form the materials which are fed back into the feedstock to produce LAS. It is acknowledged that literally, waste-plastic feedstock is also ultimately derived from the petroleum supply chain, but has an extra stage in its processing relating its constituent parts being used in different raw materials in a different context, e.g. as packaging materials. It is this extra stage which distinguishes it from what we mean by petroleum derived.

The term LAB and LAS are often used interchangeably. LAB is the material commercially handles whereas the sulphonation step to turn LAB into LAS occurs at the end is often carried out by the end user. Further, in liquid formulations the LAS is neutralised *in situ* and the weight proportions described herein refer to the protonated form.

The fragrance comprises a first perfume raw material selected from aldehydes and a second perfume raw material selected from linalool; verdox; limonene; citronellol; 3-cyclohexene-1-methanol, alpha, alpha, 4-trimethyl-, 1-acetate; tricyclo[4.2.1.1(2,5)]dec-3-en-9-ol acetate stereoisomer; and mixtures thereof.

detergent composition comprising linear alkyl benzene sulphonate (LAS) obtained from waste plastic feedstock, and a fragrance comprising a first perfume raw material (PRM1) selected from aldehydes and a second perfume raw material (PRM2) selected from

Preferably, the aldehyde is selected from octanal, undecanal, 2-methyl undecanal, beta-myrcene, butanoic acid, 2-methyl-, 1-methylethyler ether.

Preferably, the fragrance comprises from 1 to 70% wt. of the first perfume raw material. More preferably from 2 to 50% wt. of the fragrance.

Preferably, the fragrance comprises from 1 to 70% wt. of the second perfume raw material. More preferably from 2 to 50% wt. of the fragrance.

Preferably, the fragrance comprises from 0.1 to 20% wt. linanool.

Preferably, the fragrance comprises from 0.1 to 20% wt. verdox.

Preferably, the fragrance comprises from 0.1 to 20% wt. limonene, more preferably D-limonene.

Preferably, the fragrance comprises from 0.1 to 20% wt. citronellol.

Preferably, the fragrance comprises from 0.1 to 20% wt. 3-cyclohexene-1-methanol, alpha, alpha, 4-trimethyl, 1-acetate

Preferably, the fragrance comprises from 0.1 to 20% wt. tricyclo[4.2.1.1(2,5)]dec-3-en-9-ol, acetate, stereoisomer.

Preferably, the fragrance comprises from 0.1 to 20% wt. octanal.

Preferably, the fragrance comprises from 0.1 to 20% wt. undecanal.

Preferably, the fragrance comprises from 0.1 to 20% wt. 2-methyl undecanal.

Preferably, the fragrance comprises from 0.1 to 20% wt. beta-myrcene.

Preferably, the fragrance comprises from 0.1 to 20% wt. butanoic acid, 2-methyl-, 1-methylethyler ether.

Preferably, the detergent composition comprises octahydro tetramethyl acetophenone (OTNE). The OTNE is preferably present at from 1 to 40% wt., more preferably from 10 to 35% wt. of the total free fragrance present in the detergent composition. By free fragrance is meant fragrance which is not encapsulated as part of a delayed or controlled release mechanism.

In particular, we have found that performance benefits are seen with using OTNE, a specific fragrance component when using waste plastic feedstock-based LAS in the manner described. Preferably, the OTNE comprises octahydro-2',3',8',8'-tetramethyl-(2')-acetonaphthone and/or octahydro-2',3',8',8'-tetramethyl-(3')-acetonaphthone.

Preferably, the detergent composition comprises verdyl acetate. The verdyl acetate is present at from 1 to 20% wt. of the total free fragrance present in the detergent composition. By free fragrance is meant fragrance which is not encapsulated as part of a delayed or controlled release mechanism.

Preferably, the detergent composition comprises dihydromyrcenol. The dihydromyrcenol is present at from 1 to 40% wt., more preferably from 10 to 35% wt. of the total free fragrance present in the detergent composition. By free fragrance is meant fragrance which is not encapsulated as part of a delayed or controlled release mechanism.

Preferably, the laundry detergent comprises

Preferably, the detergent composition is contained in a container which comprises from 1 to 100% wt., more preferably from 20 to 100, and most preferably from 50 to 100% post-consumer recycled resin (PCR).

Preferably, the laundry liquid composition according to any preceding claim contained within a water-soluble capsule.

Preferably the detergent composition is a laundry liquid detergent composition, a powder laundry detergent composition or a liquid dishwash composition.

Liquid laundry detergents

The term “laundry detergent” in the context of this invention denotes formulated compositions intended for and capable of wetting and cleaning domestic laundry such as clothing, linens and other household textiles.

The term “linen” is often used to describe certain types of laundry items including bed sheets, pillow cases, towels, tablecloths, table napkins and uniforms. Textiles can include woven fabrics, non-woven fabrics, and knitted fabrics; and can include natural or synthetic fibres such as silk fibres, linen fibres, cotton fibres, polyester fibres, polyamide fibres such as nylon, acrylic fibres, acetate fibres, and blends thereof including cotton and polyester blends.

Examples of liquid laundry detergents include heavy-duty liquid laundry detergents for use in the wash cycle of automatic washing machines, as well as liquid fine wash and liquid colour care detergents such as those suitable for washing delicate garments (e.g. those made of silk or wool) either by hand or in the wash cycle of automatic washing machines.

The term “liquid” in the context of this invention denotes that a continuous phase or predominant part of the composition is liquid and that the composition is flowable at 15°C and above. Accordingly, the term “liquid” may encompass emulsions, suspensions, and compositions having

flowable yet stiffer consistency, known as gels or pastes. The viscosity of the composition may suitably range from about 200 to about 10,000 mPa.s at 25°C at a shear rate of 21 $sec^{-1}$. This shear rate is the shear rate that is usually exerted on the liquid when poured from a bottle. Pourable liquid detergent compositions generally have a viscosity of from 200 to 1,500 mPa.s, preferably from 100 to 800 mPa.s.

A composition according to the invention may suitably have an aqueous continuous phase. By "aqueous continuous phase" is meant a continuous phase which has water as its basis.

A composition of the invention preferably comprises from 1 to 40%, preferably from 5 to 35%, and more preferably from 7 to 24% (by weight based on the total weight of the composition) of one or more detersive surfactants selected from non-soap anionic surfactants, nonionic surfactants and mixtures thereof.

The term "detersive surfactant" in the context of this invention denotes a surfactant which provides a detersive (i.e. cleaning) effect to laundry treated as part of a domestic laundering process.

Non-soap anionic surfactants for use in the invention are typically salts of organic sulfates and sulfonates 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 such materials include alkyl sulfates, alkyl ether sulfates, alkaryl sulfonates, alpha-olefin sulfonates and mixtures thereof. The alkyl radicals preferably contain from 10 to 18 carbon atoms and may be unsaturated. The alkyl ether sulfates may contain from one to ten ethylene oxide or propylene oxide units per molecule, and preferably contain one to three ethylene oxide units per molecule. The counterion for anionic surfactants is generally an alkali metal such as sodium or potassium; or an ammoniacal counterion such as monoethanolamine, (MEA) diethanolamine (DEA) or triethanolamine (TEA). Mixtures of such counterions may also be employed.

Some alkyl sulfate surfactant (PAS) may be used, such as non-ethoxylated primary and secondary alkyl sulphates with an alkyl chain length of from 10 to 18.

Mixtures of any of the above described materials may also be used.

In a composition of the invention the total level of anionic surfactant may preferably range from 20 to 90% by weight based on the total weight of the surfactant.

Also commonly used in laundry liquid compositions are alkyl ether sulfates having a straight or branched chain alkyl group having 10 to 18, more preferably 12 to 14 carbon atoms and containing an average of 1 to 3EO units per molecule. A preferred example is sodium lauryl ether sulfate (SLES) in which the predominantly C12 lauryl alkyl group has been ethoxylated with an average of 3EO units per molecule.

Preferably, the composition comprises from 20 to 95% wt. non-ionic surfactant based on the total weight of surfactant. Nonionic surfactants for use in the invention are typically polyoxyalkylene compounds, i.e. the reaction product of alkylene oxides (such as ethylene oxide or propylene oxide or mixtures thereof) with starter molecules having a hydrophobic group and a reactive hydrogen atom which is reactive with the alkylene oxide. Such starter molecules include alcohols, acids, amides or alkyl phenols. Where the starter molecule is an alcohol, the reaction product is known as an alcohol alkoxylate. The polyoxyalkylene compounds can have a variety of block and heteric (random) structures. For example, they can comprise a single block of alkylene oxide, or they can be diblock alkoxylates or triblock alkoxylates. Within the block structures, the blocks can be all ethylene oxide or all propylene oxide, or the blocks can contain a heteric mixture of alkylene oxides. Examples of such materials include $C_8$ to $C_{22}$ alkyl phenol ethoxylates with an average of from 5 to 25 moles of ethylene oxide per mole of alkyl phenol; and aliphatic alcohol ethoxylates such as $C_8$ to $C_{18}$ primary or secondary linear or branched alcohol ethoxylates with an average of from 2 to 40 moles of ethylene oxide per mole of alcohol.

A preferred class of nonionic surfactant for use in the invention includes aliphatic $C_8$ to $C_{18}$, more preferably $C_{12}$ to $C_{15}$ primary linear alcohol ethoxylates with an average of from 3 to 20, more preferably from 5 to 10 moles of ethylene oxide per mole of alcohol.

A further class of surfactants include the alkyl poly glycosides and rhamnolipids.
Mixtures of any of the above described materials may also be used.

Preferably, the selection and amount of surfactant is such that the compositions are isotropic in nature.

**LAS**

Preferably, the alkyl chain of the LAS derived from waste-plastic feedstock comprises a mixture of chain lengths but has an average of from 8 to 16, more preferably from 10 to 14 and most preferably from 11 to 12. 11.5 to 11.7 is a particularly preferred range. Preferably the LAS contains more than 80wt% of the C10, C11, C12 and C13 alkyl chains. Preferably the weight ratio of

C10:C11 is from 1:2 to 1:5. Preferably the weight ratio of C10:C12 is from 1:2 to 1:5. Preferably the weight ratio of C10:C13 is from 1:1 to 1:3.

Preferably the level of tetralins in the LAS derived from waste-plastic feedstock is less than 8wt%, more preferably less than 0.5wt%.

Preferably the level of isoalkylbenzenes in the LAS derived from waste-plastic feedstock is less than 6wt% more preferably less than 1wt%.

Preferably, the 2-phenyl isomer content in the LAS derived from waste-plastic feedstock is at least 10% wt. of the total LAS, more preferably at least 15% and most preferably at least 20% wt. of the LAS.

Preferred surfactants include the C18 based alkyl ether sulphates, the C18 based alcohol ethoxylates and the C18 based methyl ester ethoxylates.

**C18 Alcohol Ethoxylate**

The C18 alcohol ethoxylate is of the formula:

$$R_1\text{-}O\text{-}(CH_2CH_2O)_q\text{-}H$$

where $R_1$ is selected from saturated, monounsaturated and polyunsaturated linear C18 alkyl chains and where q is from 4 to 20, preferably 5 to 14, more preferably 8 to 12. The mono-unsaturation is preferably in the 9 position of the chain, where the carbons are counted from the ethoxylate bound chain end. The double bond may be in a cis or trans configuration (oleyl or elaidyl), preferably cis. The cis or trans alcohol ethoxylate $CH_3(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_8O\text{-}(OCH_2CH_2)_nOH$, is described as C18:1(Δ9) alcohol ethoxylate. This follows the nomenclature C*X:Y*(Δ*Z*) where *X* is the number of carbons in the chain, *Y* is the number of double bonds and Δ*Z* the position of the double bond on the chain where the carbons are counted from the OH bound chain end.

Preferably, R1 is selected from saturated C18 and monounsaturated C18. As regards the C18 alcohol ethoxylate content, it is preferred that the predominant C18 moiety is C18:1, more preferably C18:1(Δ9).

Alcohol ethoxylates are discussed in the Non-ionic Surfactants: Organic Chemistry edited by Nico M. van Os (Marcel Dekker 1998), Surfactant Science Series published by CRC press. Alcohol ethoxylates are commonly referred to as alkyl ethoxylates.

Linear saturated or mono-unsaturated C20 and C22 alcohol ethoxylate may also be present. Preferably the weight fraction of sum of 'C18 alcohol ethoxylate' / 'C20 and C22 alcohol ethoxylate' is greater than 10.

Preferably the C18 alcohol ethoxylate contains less than 15wt%, more preferably less than 8wt%, most preferably less than 5wt% of the alcohol ethoxylate polyunsaturated alcohol ethoxylates. A polyunsaturated alcohol ethoxylate contains a hydrocarbon chains with two or more double bonds.

C18 alcohol ethoxylates may be synthesised by ethoxylation of an alkyl alcohol, via the reaction:

$$R_1\text{-OH} + q \text{ ethylene oxide} \rightarrow R_1\text{-O-}(CH_2CH_2O)_q\text{-H}$$

The alkyl alcohol may be produced by transesterification of the triglyceride to a methyl ester, followed by distillation and hydrogenation to the alcohol. The process is discussed in Journal of the American Oil Chemists' Society. 61 (2): 343–348 by Kreutzer, U. R. Preferred alkyl alcohol for the reaction is oleyl alcohol within an iodine value of 60 to 80, preferably 70 to 75, such alcohols are available from BASF, Cognis, Ecogreen and others.

Production of the fatty alcohol is futher discussed in Sanchez M.A. et al J.Chem.Technol.Biotechnol 2017; 92:27-92 and and Ullmann's Enzyclopaedie der technischen Chemie, Verlag Chemie, Weinheim, 4th Edition, Vol. 11, pages 436 et seq.

Preferably the ethoxylation reactions are base catalysed using NaOH, KOH, or $NaOCH_3$. Even more preferred are catalyst which provide narrower ethoxy distribution than NaOH, KOH, or $NaOCH_3$. Preferably these narrower distribution catalysts involve a Group II base such as Ba dodecanoate; Group II metal alkoxides; Group II hyrodrotalcite as described in WO2007/147866. Lanthanides may also be used. Such narrower distribution alcohol ethoxylates are available from Azo Nobel and Sasol.

Preferably the narrow ethoxy distribution has greater than 70 wt.%, more preferably greater than 80 w.t% of the alcohol ethoxylate R-O-$(CH_2CH_2O)_q$-H in the range

R-O-$(CH_2CH_2O)_x$-H to R-O-$(CH_2CH_2O)_y$-H where q is the mole average degree of ethoxylation and x and y are absolute numbers, where x = q-q/2 and y = q+q/2. For example when q=10, then greater than 70 wt.% of the alcohol ethoxylate should consist of ethoxylate with 5, 6, 7, 8, 9 10, 11, 12, 13, 14 and 15 ethoxylate groups.

However, depending on the source for the alkyl chain, it is preferred that the additional alcohol ethoxylate comprises C16 alcohol ethoxylate. More preferably, the saturated C16 alcohol ethoxylate comprises at least 90% wt. of the total C16 linear alcohol ethoxylate present.

Preferably, the proportion of monounsaturated C18 alcohol ethoxylate constitutes at least 50% wt. of the total C16 and C18 alcohol ethoxylate surfactant. However, where the level of C16 is above 30% the C18:1 level may be as low as 39%. Preferably, the C16 alcohol ethoxylate surfactant comprises at least 2% wt. and more preferably, from 4% of the total C16 and C18 alcohol ethoxylate surfactant. Preferably, the C16 saturated and C18 monounsaturated together comprise at least 75% wt. of the total alcohol ethoxylate and more preferably from 76 to 85% wt. of the total alcohol ethoxylate.

Preferably, the proportion of monounsaturated C18 constitutes at least 60% wt., most preferably at least 75 of the total C16 and C18 alcohol ethoxylate surfactant.

Preferably, the saturated C18 alcohol ethoxylate surfactant comprises up to 20% wt. and more preferably, up to 11% of the total C16 and C18 alcohol ethoxylate surfactant.

Preferably the saturated C18 content is at least 2% wt. of the total C16 and C18 alcohol ethoxylate content.

Preferably the weight fraction of C18 alcohol ethoxylate / C16 alcohol ethoxylate is greater than 1, more preferably from 2 to 100, most preferably 3 to 30. ‘C18 alcohol ethoxylate’ is the sum of all the C18 fractions in the alcohol ethoxylate and ‘C16 alcohol ethoxylate’ is the sum of all the C16 fractions in the alcohol ethoxylate.

**C18 Alcohol ether sulfates**

Preferably, the composition comprises C18 ether sulfate of the formula:

$$R_2\text{-}O\text{-}(CH_2CH_2O)_pSO_3H$$

Where $R_2$ is selected from saturated, monounsaturated and polyunsaturated linear C18 alkyl chains and where p is from 3 to 20, preferably 4 to 12, more preferably 5 to 10. The mono-unsaturation is preferably in the 9 position of the chain, where the carbons are counted from the ethoxylate bound chain end. The double bond may be in a cis or trans configuration (oleyl or elaidyl), but is preferably cis. The cis or trans ether sulfate $CH_3(CH_2)_7$-CH=CH-$(CH_2)_8O$-$(CH_2CH_2O)_nSO_3H$, is described as C18:1(Δ9) ether sulfate. This follows the nomenclature C*X:Y*(Δ*Z*) where *X* is the number of carbons in the chain, *Y* is the number of double bonds and Δ*Z* the position of the double bond on the chain where the carbons are counted from the OH bound chain end.

Preferably, R2 is selected from saturated C18 and monounsaturated C18. As regards the C18 content, it is preferred that the predominant C18 moiety is C18:1, more preferably C18:1(Δ9).

Ether sulfates are discussed in the Anionic Surfactants: Organic Chemistry edited by Helmut W. Stache (Marcel Dekker 1995), Surfactant Science Series published by CRC press.

Linear saturated or mono-unsaturated C20 and C22 ether sulfate may also be present. Preferably the weight fraction of sum of 'C18 ether sulfate' / 'C20 and C22 ether sulfate' is greater than 10.

Preferably the C18 ether sulfate contains less than 15 wt.%, more preferably less than 8 wt.%, most preferably less than 4wt% and most preferably less than 2% wt. of the ether sulfate polyunsaturated ether sulfate. A polyunsaturated ether sulfate contains a hydrocarbon chains with two or more double bonds.

Ether sulfate may be synthesised by the sulphonation of the corresponding alcohol ethoxylate. The alcohol ethoxylate may be produced by ethoxylation of an alkyl alcohol. The alkyl alcohol used to produced the alcohol ethoxylate may be produced by transesterification of the triglyceride to a methyl ester, followed by distillation and hydrogenation to the alcohol. The process is discussed in Journal of the American Oil Chemists' Society. 61 (2): 343–348 by Kreutzer, U. R. Preferred alkyl alcohol for the reaction is oleyl alcohol with an iodine value of 60 to 80, preferably 70 to 75, such alcohol are available from BASF, Cognis, Ecogreen.

The degree of polyunsaturation in the surfactant may be controlled by hydrogenation of the triglyceride as described in: A Practical Guide to Vegetable Oil Processing (Gupta M.K. Academic Press 2017). Distillation and other purification techniques may be used.

Ethoxylation reactions are described in Non-Ionic Surfactant Organic Chemistry (N. M. van Os ed), Surfactant Science Series Volume 72, CRC Press.

Preferably the ethoxylation reactions are base catalysed using NaOH, KOH, or $NaOCH_3$. Even more preferred are catalyst which provide narrower ethoxy distribution than NaOH, KOH, or $NaOCH_3$. Preferably these narrower distribution catalysts involve a Group II base such as Ba dodecanoate; Group II metal alkoxides; Group II hyrodrotalcite as described in WO2007/147866. Lanthanides may also be used. Such narrower distribution alcohol ethoxylates are available from Azo Nobel and Sasol.

Preferably the narrow ethoxy distribution has greater than 70 wt.%, more preferably greater than 80 w.t% of the ether sulfate $R_2$-O-$(CH_2CH_2O)_pSO_3H$ in the range $R_2$-O-$(CH_2CH_2O)_zSO_3H$ to $R_2$-O-$(CH_2CH_2O)_wSO_3H$ where q is the mole average degree of ethoxylation and x and y are absolute numbers, where z = p-p/2 and w = p+p/2. For example when p=6, then greater than 70 wt.% of the ether sulfate should consist of ether sulfate with 3, 4, 5, 6, 7, 8, 9 ethoxylate groups.

The ether sulfate weight is calculated as the protonated form: $R_2$-O-$(CH_2CH_2O)_pSO_3H$. In the formulation it will be present as the ionic form $R_2$-O-$(CH_2CH_2O)_pSO_3^-$ with a corresponding counter ion, preferred counter ions are group I and II metals, amines, most preferably sodium.

The composition may also comprise C16 alkyl ether sulphate. This may be a consequence of active addition of C16 or by way of a component of the sourcing of the C18 raw material.

More preferably, the saturated C16 comprises at least 90% wt. of the C16 content linear alkyl.

Preferably, the proportion of monounsaturated C18 constitutes at least 50% wt. of the total C16 and C18 alkyl ether sulphate surfactant. However, where the level of C16 is above 30% the C18:1 level may be as low as 39%. Preferably, the C16 alcohol ether sulphate surfactant comprises at least 2% wt. and more preferably, from 4% of the total C16 and C18 alcohol ether sulphate surfactant. Preferably, the C16 saturated and C18 monounsaturated together comprise at least 75% wt. of the total alcohol ether sulphate and more preferably from 76 to 85% wt. of the total alcohol ether sulphate.

More preferably, the proportion of monounsaturated C18 constitutes at least 60% wt., most preferably at least 75 of the total C16 and C18 alkyl ether sulphate surfactant.

Preferably, the C16 alkyl ether sulphate surfactant comprises at least 2% wt. and more preferably, from 4% of the total C16 and C18 alkyl ether sulphate surfactant.

Preferably, the saturated C18 alkyl ether sulphate surfactant comprises up to 20% wt. and more preferably, up to11% of the total C16 and C18 alkyl ether sulphate surfactant. Preferably the saturated C18 content is at least 2% wt. of the total C16 and C18 alkyl ether sulphate content.

Where the composition comprises a mixture of the C16/18 sourced material for the alkyl ether sulphate as well as the more traditional C12 alkyl chain length materials it is preferred that the total C16/18 alkyl ether sulphate content should comprise at least 10% wt. of the total alkyl ether sulphate, more preferably at least 50%, even more preferably at least 70%, especially preferably at least 90% and most preferably at least 95% of alkyl ether sulphate in the composition.

Preferably, the weight ratio of total non-ionic surfactant to total alkyl ether sulphate surfactant (wt. non-ionic / wt. alkyl ether sulphate) is from 0.5 to 2, preferably from 0.7 to 1.5, most preferably 0.9 to 1.1.

Preferably, the weight ratio of total C16/18 non-ionic surfactant, to total alkyl ether sulphate surfactant (wt. non-ionic / wt. alkyl ether sulphate) is from 0.5 to 2, preferably from 0.7 to 1.5, most preferably 0.9 to 1.1.

Preferably, the weight ratio of total non-ionic surfactant to total C16/18 alkyl ether sulphate surfactant (wt. non-ionic / wt. alkyl ether sulphate) is from 0.5 to 2, preferably from 0.7 to 1.5, most preferably 0.9 to 1.1.

Preferably, the weight ratio of total C18:1 non-ionic surfactant to total C18:1 alkyl ether sulphate surfactant (wt. non-ionic / wt. alkyl ether sulphate) is from 0.5 to 2, preferably from 0.7 to 1.5, most preferably 0.9 to 1.1.

Preferably, the weight ratio of total non-ionic surfactant to linear alkyl benzene sulphonate, where present, (wt. non-ionic/ wt. linear alkyl benzene sulphonate) is from 0.1 to 2, preferably 0.3 to 1, most preferably 0.45 to 0.85.

Preferably, the weight ratio of total C16/18 non-ionic surfactant to linear alkyl benzene sulphonate, where present, (wt. non-ionic/ wt. linear alkyl benzene sulphonate) is from 0.1 to 2, preferably 0.3 to 1, most preferably 0.45 to 0.85.

**Source of alkyl chains**

The alkyl chain of C16/18 surfactant whether an alcohol ethoxylate or an alkyl ether sulphate is preferably obtained from a renewable source, preferably from a triglyceride. A renewable source is one where the material is produced by natural ecological cycle of a living species, preferably by a plant, algae, fungi, yeast or bacteria, more preferably plants, algae or yeasts.

Preferred plant sources of oils are rapeseed, sunflower, maze, soy, cottonseed, olive oil and trees. The oil from trees is called tall oil. Most preferably Palm and Rapeseed oils are the source.

Algal oils are discussed in Energies 2019, 12, 1920 *Algal Biofuels: Current Status and Key Challenges* by Saad M.G. et al. A process for the production of triglycerides from biomass using yeasts is described in Energy Environ. Sci., 2019,12, 2717 *A sustainable, high-performance process for the economic production of waste-free microbial oils that can replace plant-based equivalents* by Masri M.A. et al.

Non edible plant oils may be used and are preferably selected from the fruit and seeds of Jatropha curcas, Calophyllum inophyllum, Sterculia feotida, Madhuca indica (mahua), Pongamia glabra (koroch seed), Linseed, Pongamia pinnata (karanja), Hevea brasiliensis (Rubber seed), Azadirachta indica (neem), Camelina sativa, Lesquerella fendleri, Nicotiana tabacum (tobacco), Deccan hemp, Ricinus communis L.(castor), Simmondsia chinensis (Jojoba), Eruca sativa. L., Cerbera odollam (Sea mango), Coriander (Coriandrum sativum L.), Croton megalocarpus, Pilu, Crambe, syringa, Scheleichera triguga (kusum), Stillingia, Shorea robusta (sal), Terminalia belerica roxb, Cuphea, Camellia, Champaca, Simarouba glauca, Garcinia indica, Rice bran, Hingan (balanites), Desert date, Cardoon, Asclepias syriaca (Milkweed), Guizotia abyssinica, Radish Ethiopian mustard, Syagrus, Tung, Idesia polycarpa var. vestita, Alagae, Argemone mexicana L. (Mexican prickly poppy, Putranjiva roxburghii (Lucky bean tree), Sapindus mukorossi (Soapnut), M. azedarach (syringe),Thevettia peruviana (yellow oleander), Copaiba, Milk bush, Laurel, Cumaru, Andiroba, Piqui, B. napus, Zanthoxylum bungeanum.

**MOULDED ARTICLE**

Preferably, the composition is stored in a moulded article. Preferably, such moulded article comprises post-consumer recycled material. The moulded article is preferably a container such as a bottle for containing a fluid product. Preferred fluid products include cleaning compositions for the home and body and which are usually fragranced and comprise surfactant components. Having an improved container material is thus highly advantageous since PCR often interacts with such

sensitive components. Further, it is extremely undesirable that such containers are prone to stress damage.

The moulded article is preferably blow moulded. Blow moulding involves the formation of a parison or preform which is placed and clamped into the mould. Air is passed into the parison/preform to expand the parison/preform such that it expands to fill the space in the mould. Once the plastic has hardened sufficiently, the mould is de-coupled and the moulded article is removed.

Preferably, the weight ratio between PCR and any non-recycled material content in the moulded article is from 1:9 to 100:0 but this depends on the physical structure of the article. For example, the article may comprise additional features such as a shrink-wrap outer skin, a cap, a pump assembly all of which may not comprise any PCR.

Preferably, the moulded article comprises additives to improve the performance of the article. Examples include HDPE, LLDPE and LLDP.

For example, where the article comprises a monolayer it is preferred that the weight ratio between the additive (for example HDPE and/or LLDPE and/or LDPE) and the PCR in the blow moulded article monolayer is from 5:95 to 30:70. However, where a multilayer article is provided and which only one layer comprises additive and PCR it is preferred that the weight ratio between the additive and the PCR in the individual layer is from 1:99 to 30:1 but the total proportion of additive in the article as a whole will depend on the weight ratio between the additive with PCR layer and any other layer used.

Typical additional layers may include PCR or virgin polyethylene as desired. For example, where an improved aesthetic is required the outer layer may comprise virgin polymer whereas the inner layer may comprise HDPE and/or LLDPE and/or LDPE with the PCR.

It is also of course possible that other materials are included with the HDPE/PCR such that in one layer the additive/PCR constitutes from 70 to 100% by weight of the layer and more preferably from 95 to 100% of the layer.

Preferably the outer and/or inner layer comprises a colourant masterbatch. More preferably, the outer layer comprises a colourant masterbatch. By “colourant masterbatch” it is a meant a mixture in which pigments are dispersed at high concentration in a carrier material. The colorant masterbatch is used to impart colour to the article.

The carrier may be a biobased plastic or a petroleum-based plastic, or a biobased oil or a petroleum-based oil or made of post-consumer resin (PCR).

Nonlimiting examples of the carrier include bio-derived or oil derived polyethylene (e.g, LLDPE, LDPE, HDPE), bio-derived oil (e.g., olive oil, rapeseed oil, peanut oil), petroleum-derived oil, recycled oil, bio-derived or petroleum derived polyethylene terephthalate, polypropylene, recycled high density polyethylene (rHDPE), recycled low density polyethylene (rLDPE). Preferably the carrier is recycled high density polyethylene (rHDPE) or recycled low density polyethylene (rLDPE).

When it is desired that all the layers are made of 100% of PCR, the carrier is also preferably selected from PCR. Similarly, when it is desired that a layer has a 100% of a specific PCR, the carrier is preferably selected from the same PCR.

The pigment, when present, of the masterbatch is a NIR detectable pigment. Carbon black is not preferred in the scope of the present invention. The NIR detectable pigment is preferably black. The pigment is typically made of a combination of known colours.

By consumer acceptable black, it may be defined as the colour measured using a reflectometer and expressed as the CIE L*a*b* values and the values of L being less than 25, preferably less than 23, more preferably less than 20, even more preferably less than 15, still more preferably less than 12 or even less than 10, the values of a being in the ranges of -5 to 5, preferably -2 to 3, more preferably 0 to 2 and the values of b being in the ranges of -10 and 10, preferably -8 to 5.

By NIR detectable pigment is meant detectable by Near Infrared (NIR) spectroscopy.

The pigment of the carrier may include, for example, an inorganic pigment, an organic pigment, a polymeric resin, or a mixture thereof.

Optionally, the colourant masterbatch can further include one or more additives. Nonlimiting examples of additives include slip agents, UV absorbers, nucleating agents, UV stabilizers, heat stabilizers, clarifying agents, fillers, brighteners, process aids, perfumes, flavors, and a mixture thereof.

Such NIR detectable pigments are known in the art and are provided by various suppliers such as Clariant, globally and Colourtone Masterbatch Ltd. in Europe.

The moulded article according to the invention is preferably a container, e.g. for a bottle; in particular the article according to the invention is a non-food grade container.

## FRAGRANCES

Fragrance components are well known in the art and are preferably incorporated into compositions described herein such that the level of fragrance in totality is from1 to 5 wt.%.

Octahydrotetramethyl acetophenone (OTNE) is a desirable synthetic fragrance component (or perfume raw material) which delivers a particularly attractive sandalwood and cedarwood fragrance effect to consumables.

OTNE is the abbreviation for the fragrance material with CAS numbers 68155-66-8, 54464-57-2 and 68155-67-9 and EC List number 915-730-3. Preferably the OTNE is present as a multi-constituent isomer mixture containing:

- 1-(1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-naphthyl)ethan-1-one (CAS 54464-57-2)
- 1-(1,2,3,5,6,7,8,8a-octahydro-2,3,8,8-tetramethyl-2-naphthyl)ethan-1-one (CAS 68155-66-8)
- 1-(1,2,3,4,6,7,8,8a-octahydro-2,3,8,8-tetramethyl-2-naphthyl)ethan-1-one (CAS 68155-67-9)

More particularly, the invention has to do with amber-like fragrance compositions for use in perfumery composed of octahydro-2',3',8',8'-tetramethyl-(2' or 3')-acetonaphthones in which a majority of said acetonaphthones contains the double bond in the 9'-10' position.
Such OTNE and its method for manufacture is described fully in US3907321 (IFF).
The fragrance Molecule 01 is a specific isomer of OTNE, commercially available from IFF. Another commercially available fragrance Escentric 01 contains OTNE but also ambroxan, pink pepper, green lime with balsamic notes like benzoin mastic and incense. Typically, commercially available fragrance raw materials comprise from 1 to 8% wt. of the fragrance raw material OTNE.

Preferably, the detergent composition comprises 0.01 to 0.2% wt. of the composition OTNE as described above. More preferably, from 0.07 to 0.15% wt. of the composition OTNE.

Preferably, the fragrance comprises a fragrance component selected from the benzene, toluene, xylene (BTX) feedstock class. More preferably, the fragrance component is selected from 2-phenyl ethanol, phenoxanol and mixtures thereof.

Preferably, the fragrance comprises a fragrance component selected from the cyclododecanone feedstock class. More preferably, the fragrance component is habolonolide.

Preferably, the fragrance comprises a fragrance component selected from the phenolics feedstock class. More preferably, the fragrance component is hexyl salicylate.

Preferably, the fragrance comprises a fragrance component selected from the C5 blocks or oxygen containing heterocycle moiety feedstock class. More preferably, the fragrance component is selected from gamma decalactone, methyl dihydrojasmonate and mixtures thereof.

Preferably, the fragrance comprises a fragrance component selected from the terpenes feedstock class. More preferably, the fragrance component is selected from dihydromycernol, linalool, terpinolene, camphor, citronellol and mixtures thereof.

Preferably, the fragrance comprises a fragrance component selected from the alkyl alcohols feedstock class. More preferably, the fragrance component is ethyl-2-methylbutyrate.

Preferably, the fragrance comprises a fragrance component selected from the diacids feedstock class. More preferably, the fragrance component is ethylene brassylate.

Preferably, the fragrance component listed above is present in the final detergent composition at from 0.0001 to 1% by wt. of the composition.

Preferably, the detergent composition comprises limonene, preferably present at from 1 to 40% wt., more preferably from 2 to 10% wt. of the total free fragrance present in the detergent composition.

Most preferably when limonene is present verdox™ and/or rose oxide is also present, preferably at 0.1 to 10wt% of the perfume.

**Fatty Acid**

Preferably, fatty acid is present at from 0.1 to 20% wt. of the composition (as measured with reference to the acid added to the composition), more preferably from 1 to 12% wt. and most preferably 6 to 8% wt.

Suitable fatty acids in the context of this invention include aliphatic carboxylic acids of formula RCOOH, where R is a linear or branched alkyl or alkenyl chain containing from 6 to 24, more

preferably 10 to 22, most preferably from 12 to 18 carbon atoms and 0 or 1 double bond. Preferred examples of such materials include saturated C12-18 fatty acids such as lauric acid, myristic acid, palmitic acid or stearic acid; and fatty acid mixtures in which 50 to 100% (by weight based on the total weight of the mixture) consists of saturated C12-18 fatty acids. Such mixtures may typically be derived from natural fats and/or optionally hydrogenated natural oils (such as coconut oil, palm kernel oil or tallow).

The fatty acids may be present in the form of their sodium, potassium or ammonium salts and/or in the form of soluble salts of organic bases, such as mono-, di- or triethanolamine.

Mixtures of any of the above described materials may also be used.

For formula accounting purposes, in the formulation, fatty acids and/or their salts (as defined above) are not included in the level of surfactant or in the level of builder.

**Sequestrant**

The detergent compositions may also preferably comprise a sequestrant material. Examples include the alkali metal citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other examples are DEQUEST™, organic phosphonate type sequestering agents sold by Monsanto and alkanehydroxy phosphonates.

A preferred sequestrant is Dequest(R) 2066 (Diethylenetriamine penta(methylene phosphonic acid or Heptasodium DTPMP). HEDP (1 -Hydroxyethylidene -1,1,-diphosphonic acid), is preferably not present.

In a preferred embodiment the composition comprises fatty acid and sequestrant.
The composition according to the invention is a low aqueous composition. Preferably, the composition comprises less than 15% wt. water, more preferably less than 10% wt. water.

**PRESERVATIVE**

Food preservatives are discussed In Food Chemistry (Belitz H.-D., Grosch W., Schieberle), 4th edition Springer.

The formulation contains a preservative or a mixture of preservatives, selected from benzoic acid and salts thereof, alkylesters of p-hydroxybenzoic acid and salts thereof, sorbic acid, diethyl pyrocarbonate, dimethyl pyrocarbonate, preferably benzoic acid and salts thereof, most preferably sodium benzoate. The preservative is present at 0.01 to 3wt%, preferably 0.3wt% to 1.5w%. Weights are calculated for the protonated form.

## CLEANING POLYMERS

Anti-redeposition polymers stabilise the soil in the wash solution thus preventing redeposition of the soil. Suitable soil release polymers for use in the invention include alkoxylated polyethyleneimines. Polyethyleneimines are materials composed of ethylene imine units $-CH_2CH_2NH-$ and, where branched, the hydrogen on the nitrogen is replaced by another chain of ethylene imine units. Preferred alkoxylated polyethyleneimines for use in the invention have a polyethyleneimine backbone of about 300 to about 10000 weight average molecular weight ($M_w$). The polyethyleneimine backbone may be linear or branched. It may be branched to the extent that it is a dendrimer. The alkoxylation may typically be ethoxylation or propoxylation, or a mixture of both. Where a nitrogen atom is alkoxylated, a preferred average degree of alkoxylation is from 10 to 30, preferably from 15 to 25 alkoxy groups per modification. A preferred material is ethoxylated polyethyleneimine, with an average degree of ethoxylation being from 10 to 30, preferably from 15 to 25 ethoxy groups per ethoxylated nitrogen atom in the polyethyleneimine backbone.

Mixtures of any of the above described materials may also be used.

A composition of the invention will preferably comprise from 0.025 to 8% wt. of one or more anti-redeposition polymers such as, for example, the alkoxylated polyethyleneimines which are described above.

## SOIL RELEASE POLYMERS

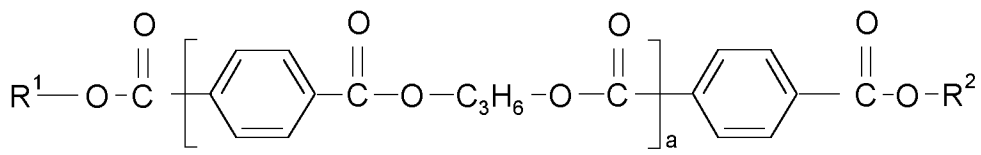
Soil release polymers help to improve the detachment of soils from fabric by modifying the fabric surface during washing. The adsorption of a SRP over the fabric surface is promoted by an affinity between the chemical structure of the SRP and the target fibre.

SRPs for use in the invention may include a variety of charged (e.g. anionic) as well as non-charged monomer units and structures may be linear, branched or star-shaped. The SRP structure may also include capping groups to control molecular weight or to alter polymer properties such as surface activity. The weight average molecular weight ($M_w$) of the SRP may suitably range from about 1000 to about 20,000 and preferably ranges from about 1500 to about 10,000.

SRPs for use in the invention may suitably be selected from copolyesters of dicarboxylic acids (for example adipic acid, phthalic acid or terephthalic acid), diols (for example ethylene glycol or propylene glycol) and polydiols (for example polyethylene glycol or polypropylene glycol). The co-polyester may also include monomeric units substituted with anionic groups, such as for example sulfonated isophthaloyl units. Examples of such materials include oligomeric esters produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, dimethyl terephthalate ("DMT"), propylene glycol ("PG") and poly(ethyleneglycol) ("PEG"); partly- and fully-anionic-end-capped oligomeric esters such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; non-ionic-capped block polyester oligomeric compounds such as those produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate, and copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate.

Other types of SRP for use in the invention include cellulosic derivatives such as hydroxyether cellulosic polymers, $C_1$-$C_4$ alkylcelluloses and $C_4$ hydroxyalkyl celluloses; polymers with poly(vinyl ester) hydrophobic segments such as graft copolymers of poly(vinyl ester), for example $C_1$-$C_6$ vinyl esters (such as poly(vinyl acetate)) grafted onto polyalkylene oxide backbones; poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate; and polyester-polyamide polymers prepared by condensing adipic acid, caprolactam, and polyethylene glycol.

Preferred SRPs for use in the invention include copolyesters formed by condensation of terephthalic acid ester and diol, preferably 1,2 propanediol, and further comprising an end cap formed from repeat units of alkylene oxide capped with an alkyl group. Examples of such materials have a structure corresponding to general formula (I):



(I)

in which $R^1$ and $R^2$ independently of one another are $X\text{-}(OC_2H_4)_n\text{-}(OC_3H_6)_m$;
in which X is $C_{1\text{-}4}$ alkyl and preferably methyl;
n is a number from 12 to 120, preferably from 40 to 50;
m is a number from 1 to 10, preferably from 1 to 7; and
a is a number from 4 to 9.

Because they are averages, m, n and a are not necessarily whole numbers for the polymer in bulk. Mixtures of any of the above described materials may also be used.

The overall level of SRP, when included, may range from 0.1 to 10%, depending on the level of polymer intended for use in the final diluted composition and which is desirably from 0.3 to 7%, more preferably from 0.5 to 5% (by weight based on the total weight of the diluted composition).

Suitable soil release polymers are described in greater detail in U. S. Patent Nos. 5,574,179; 4,956,447; 4,861,512; 4,702,857, WO 2007/079850 and WO2016/005271. If employed, soil release polymers will typically be incorporated into the liquid laundry detergent compositions herein in concentrations ranging from 0.01 percent to 10 percent, more preferably from 0.1 percent to 5 percent, by weight of the composition.

## HYDROTROPES

A composition of the invention may incorporate non-aqueous carriers such as hydrotropes, co-solvents and phase stabilizers. Such materials are typically low molecular weight, water-soluble or water-miscible organic liquids such as C1 to C5 monohydric alcohols (such as ethanol and n- or i-propanol); C2 to C6 diols (such as monopropylene glycol and dipropylene glycol); C3 to C9 triols (such as glycerol); polyethylene glycols having a weight average molecular weight ($M_w$) ranging from about 200 to 600; C1 to C3 alkanolamines such as mono-, di- and triethanolamines; and alkyl aryl sulfonates having up to 3 carbon atoms in the lower alkyl group (such as the sodium and potassium xylene, toluene, ethylbenzene and isopropyl benzene (cumene) sulfonates). Mixtures of any of the above described materials may also be used.

Non-aqueous carriers, are preferably included, may be present in an amount ranging from 1 to 50%, preferably from 10 to 30%, and more preferably from 15 to 25% (by weight based on the total weight of the composition). The level of hydrotrope used is linked to the level of surfactant and it is desirable to use hydrotrope level to manage the viscosity in such compositions. The preferred hydrotropes are monopropylene glycol and glycerol.

## COSURFACTANTS

A composition of the invention may contain one or more cosurfactants (such as amphoteric (zwitterionic) and/or cationic surfactants) in addition to the non-soap anionic and/or nonionic detersive surfactants described above.

Specific cationic surfactants include C8 to C18 alkyl dimethyl ammonium halides and derivatives thereof in which one or two hydroxyethyl groups replace one or two of the methyl groups, and mixtures thereof. Cationic surfactant, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

Specific amphoteric (zwitterionic) surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulfobetaines (sultaines), alkyl glycinates, alkyl carboxyglycinates, alkyl amphoacetates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, having alkyl radicals containing from about 8 to about 22 carbon atoms preferably selected from C12, C14, C16 ,C18 and C18:1, the term "alkyl" being used to include the alkyl portion of higher acyl radicals. Amphoteric (zwitterionic) surfactant, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

Mixtures of any of the above described materials may also be used.

## FLUORESCENT AGENTS

It may be advantageous to include fluorescer in the compositions. 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 to 2 wt %, more preferably 0.01 to 0.5 wt % the composition.

Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal ® CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra, Tinopal 5BMGX, and Blankophor ® HRH, and Pyrazoline compounds, e.g. Blankophor SN.

Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[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-sulfoslyryl)biphenyl.

Most preferably the fluoescer is a di-styryl biphenyl compound, preferably sodium 2,2'-([1,1'-biphenyl]-4,4'-diylbis(ethene-2,1-diyl))dibenzenesulfonate (CAS-No 27344-41-8).

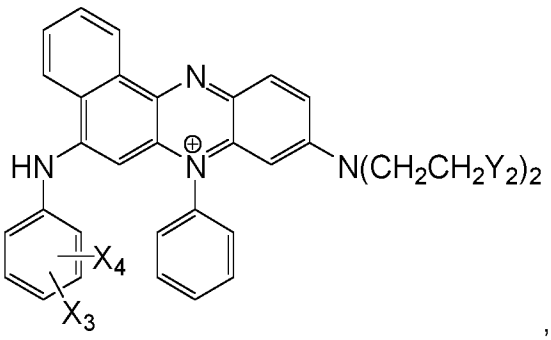
## SHADING DYES

Shading dye can be used to improve the performance of the compositions. Preferred dyes are violet or blue. It is believed that the deposition on fabrics of a low level of a dye of these shades, masks yellowing of fabrics. A further advantage of shading dyes is that they can be used to mask any yellow tint in the composition itself.

Shading dyes are well known in the art of laundry liquid formulation.

Suitable and preferred classes of dyes include direct dyes, acid dyes, hydrophobic dyes, basic dyes, reactive dyes and dye conjugates. Preferred examples are Disperse Violet 28, Acid Violet 50, anthraquinone dyes covalently bound to ethoxylate or propoxylated polyethylene imine as described in WO2011/047987 and WO 2012/119859.

alkoxylated mono-azo thiophenes, dye with CAS-No 72749-80-5, acid blue 59, and the phenazine dye selected from:




,

wherein:

$X_3$ is selected from: -H; -F; -$CH_3$; -$C_2H_5$; -$OCH_3$; and, –$OC_2H_5$;

$X_4$ is selected from: -H; -$CH_3$; -$C_2H_5$; -$OCH_3$; and, –$OC_2H_5$;

$Y_2$ is selected from: –OH; -$OCH_2CH_2OH$; -$CH(OH)CH_2OH$; -$OC(O)CH_3$; and, $C(O)OCH_3$.

Alkoxylated thiophene dyes are discussed in WO2013/142495 and WO2008/087497.

The shading dye is preferably present is present in the composition in range from 0.0001 to 0.1wt %. 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.

## EXTERNAL STRUCTURANTS

Compositions of the invention may have their rheology further modified by use of one or more external structurants which form a structuring network within the composition. Examples of such materials include hydrogenated castor oil, microfibrous cellulose and citrus pulp fibre. The presence of an external structurant may provide shear thinning rheology and may also enable materials such as encapsulates and visual cues to be suspended stably in the liquid.

## ENZYMES

A composition of the invention may comprise an effective amount of one or more enzyme selected from the group comprising, pectate lyase, protease, amylase, cellulase, lipase, mannanase and mixtures thereof. The enzymes are preferably present with corresponding enzyme stabilizers.

## MICROCAPSULES

One type of microparticle suitable for use in the invention is a microcapsule.

Microencapsulation may be defined as the process of surrounding or enveloping one substance within another substance on a very small scale, yielding capsules ranging from less than one micron to several hundred microns in size. The material that is encapsulated may be called the core, the active ingredient or agent, fill, payload, nucleus, or internal phase. The material encapsulating the core may be referred to as the coating, membrane, shell, or wall material.

Microcapsules typically have at least one generally spherical continuous shell surrounding the core. The shell may contain pores, vacancies or interstitial openings depending on the materials and encapsulation techniques employed. Multiple shells may be made of the same or different encapsulating materials, and may be arranged in strata of varying thicknesses around the core. Alternatively, the microcapsules may be asymmetrically and variably shaped with a quantity of smaller droplets of core material embedded throughout the microcapsule.

The shell may have a barrier function protecting the core material from the environment external to the microcapsule, but it may also act as a means of modulating the release of core materials such as fragrance. Thus, a shell may be water soluble or water swellable and fragrance release may be actuated in response to exposure of the microcapsules to a moist environment. Similarly, if a shell is temperature sensitive, a microcapsule might release fragrance in response to elevated temperatures. Microcapsules may also release fragrance in response to shear forces applied to the surface of the microcapsules.

A preferred type of polymeric microparticle suitable for use in the invention is a polymeric core-shell microcapsule in which at least one generally spherical continuous shell of polymeric material surrounds a core containing the fragrance formulation (f2). The shell will typically comprise at most 20% by weight based on the total weight of the microcapsule. The fragrance formulation (f2) will typically comprise from about 10 to about 60% and preferably from about 20 to about 40% by weight based on the total weight of the microcapsule. The amount of fragrance (f2) may be measured by taking a slurry of the microcapsules, extracting into ethanol and measuring by liquid chromatography.

Polymeric core-shell microcapsules for use in the invention may be prepared using methods known to those skilled in the art such as coacervation, interfacial polymerization, and polycondensation.

The process of coacervation typically involves encapsulation of a generally water-insoluble core material by the precipitation of colloidal material(s) onto the surface of droplets of the material. Coacervation may be simple e.g. using one colloid such as gelatin, or complex where two or possibly more colloids of opposite charge, such as gelatin and gum arabic or gelatin and carboxymethyl cellulose, are used under carefully controlled conditions of pH, temperature and concentration.

Interfacial polymerisation typically proceeds with the formation of a fine dispersion of oil droplets (the oil droplets containing the core material) in an aqueous continuous phase. The dispersed droplets form the core of the future microcapsule and the dimensions of the dispersed droplets directly determine the size of the subsequent microcapsules.

Microcapsule shell-forming materials (monomers or oligomers) are contained in both the dispersed phase (oil droplets) and the aqueous continuous phase and they react together at the phase interface to build a polymeric wall around the oil droplets thereby to encapsulate the droplets and form core-shell microcapsules. An example of a core-shell microcapsule produced by this method is a polyurea microcapsule with a shell formed by reaction of diisocyanates or polyisocyanates with diamines or polyamines.

Polycondensation involves forming a dispersion or emulsion of the core material in an aqueous solution of precondensate of polymeric materials under appropriate conditions of agitation to produce capsules of a desired size, and adjusting the reaction conditions to cause condensation of the precondensate by acid catalysis, resulting in the condensate separating from solution and surrounding the dispersed core material to produce a coherent film and the desired microcapsules.

An example of a core-shell microcapsule produced by this method is an aminoplast microcapsule with a shell formed from the polycondensation product of melamine (2,4,6-triamino-1,3,5-triazine) or urea with formaldehyde. Suitable cross-linking agents (e.g. toluene diisocyanate, divinyl benzene, butanediol diacrylate) may also be used and secondary wall polymers may also be used as appropriate, e.g. anhydrides and their derivatives, particularly polymers and co-polymers of maleic anhydride.

One example of a preferred polymeric core-shell microcapsule for use in the invention is an aminoplast microcapsule with an aminoplast shell surrounding a core containing the fragrance formulation (f2). More preferably such an aminoplast shell is formed from the polycondensation product of melamine with formaldehyde.

Polymeric microparticles suitable for use in the invention will generally have an average particle size between 100 nanometers and 50 microns. Particles larger than this are entering the visible range. Examples of particles in the sub-micron range include latexes and mini-emulsions with a typical size range of 100 to 600 nanometers. The preferred particle size range is in the micron range. Examples of particles in the micron range include polymeric core-shell microcapsules (such as those further described above) with a typical size range of 1 to 50 microns, preferably 5 to 30 microns. The average particle size can be determined by light scattering using a Malvern Mastersizer with the average particle size being taken as the median particle size D (0.5) value. The particle size distribution can be narrow, broad or multimodal. If necessary, the microcapsules as initially produced may be filtered or screened to produce a product of greater size uniformity.

Polymeric microparticles suitable for use in the invention may be provided with a deposition aid at the outer surface of the microparticle. Deposition aids serve to modify the properties of the exterior of the microparticle, for example to make the microparticle more substantive to a desired substrate. Desired substrates include cellulosics (including cotton) and polyesters (including those employed in the manufacture of polyester fabrics).

The deposition aid may suitably be provided at the outer surface of the microparticle by means of covalent bonding, entanglement or strong adsorption. Examples include polymeric core-shell microcapsules (such as those further described above) in which a deposition aid is attached to the outside of the shell, preferably by means of covalent bonding. While it is preferred that the deposition aid is attached directly to the outside of the shell, it may also be attached via a linking species.

Deposition aids for use in the invention may suitably be selected from polysaccharides having an affinity for cellulose. Such polysaccharides may be naturally occurring or synthetic and may have an intrinsic affinity for cellulose or may have been derivatised or otherwise modified to have an affinity for cellulose. Suitable polysaccharides have a 1-4 linked β glycan (generalised sugar) backbone structure with at least 4, and preferably at least 10 backbone residues which are β1-4 linked, such as a glucan backbone (consisting of β1-4 linked glucose residues), a mannan backbone (consisting of β1-4 linked mannose residues) or a xylan backbone (consisting of β1-4 linked xylose residues). Examples of such β1-4 linked polysaccharides include xyloglucans, glucomannans, mannans, galactomannans, β(1-3),(1-4) glucan and the xylan family incorporating glucurono-, arabino- and glucuronoarabinoxylans. Preferred β1-4 linked polysaccharides for use in the invention may be selected from xyloglucans of plant origin, such as pea xyloglucan and tamarind seed xyloglucan (TXG) (which has a β1-4 linked glucan backbone with side chains of α-D xylopyranose and β-D-galactopyranosyl-(1-2)-α-D-xylo-pyranose, both 1-6 linked to the backbone); and galactomannans of plant origin such as loc ust bean gum (LBG) (which has a mannan backbone of β1-4 linked mannose residues, with single unit galactose side chains linked α1-6 to the backbone).

Also suitable are polysaccharides which may gain an affinity for cellulose upon hydrolysis, such as cellulose mono-acetate; or modified polysaccharides with an affinity for cellulose such as hydroxypropyl cellulose, hydroxypropyl methylcellulose, hydroxyethyl methylcellulose, hydroxypropyl guar, hydroxyethyl ethylcellulose and methylcellulose.

Deposition aids for use in the invention may also be selected from phthalate containing polymers having an affinity for polyester. Such phthalate containing polymers may have one or more nonionic hydrophilic segments comprising oxyalkylene groups (such as oxyethylene, polyoxyethylene, oxypropylene or polyoxypropylene groups), and one or more hydrophobic segments comprising terephthalate groups. Typically, the oxyalkylene groups will have a degree of polymerization of from 1 to about 400, preferably from 100 to about 350, more preferably from 200 to about 300. A suitable example of a phthalate containing polymer of this type is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide terephthalate.

Mixtures of any of the above described materials may also be suitable.

Deposition aids for use in the invention will generally have a weight average molecular weight ($M_w$) in the range of from about 5 kDa to about 500 kDa, preferably from about 10 kDa to about 500 kDa and more preferably from about 20 kDa to about 300 kDa.

One example of a particularly preferred polymeric core-shell microcapsule for use in the invention is an aminoplast microcapsule with a shell formed by the polycondensation of melamine with formaldehyde; surrounding a core containing the fragrance formulation (f2); in which a deposition aid is attached to the outside of the shell by means of covalent bonding. The preferred deposition aid is selected from β1-4 linked polysaccharides, and in particular the xyloglucans of plant origin, as are further described above.

The present inventors have surprisingly observed that it is possible to reduce the total level of fragrance included in the composition of the invention without sacrificing the overall fragrance experience delivered to the consumer at key stages in the laundry process. A reduction in the total level of fragrance is advantageous for cost and environmental reasons.

Accordingly, the total amount of fragrance formulation (f1) and fragrance formulation (f2) in the composition of the invention suitably ranges from 0.5 to 1.4%, preferably from 0.5 to 1.2%, more preferably from 0.5 to 1% and most preferably from 0.6 to 0.9% (by weight based on the total weight of the composition).

The weight ratio of fragrance formulation (f1) to fragrance formulation (f2) in the composition of the invention preferably ranges from 60:40 to 45:55. Particularly good results have been obtained at a weight ratio of fragrance formulation (f1) to fragrance formulation (f2) of around 50:50.

The fragrance (f1) and fragrance (f2) are typically incorporated at different stages of formation of the composition of the invention. Typically, the discrete polymeric microparticles (e.g. microcapsules) entrapping fragrance formulation (f2) are added in the form of a slurry to a warmed base formulation comprising other components of the composition (such as surfactants and solvents). Fragrance (f1) is typically post-dosed later after the base formulation has cooled.

## FURTHER OPTIONAL INGREDIENTS

A composition of the invention may contain further optional ingredients to enhance performance and/or consumer acceptability. Examples of such ingredients include foam boosting agents, preservatives (e.g. bactericides), polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, ironing aids, colorants, pearlisers and/or opacifiers, and shading dye. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally, these optional ingredients are included individually at an amount of up to 5% (by weight based on the total weight of the diluted composition) and so adjusted depending on the dilution ratio with water.

PARTICULATE LAUNDRY DETERGENT COMPOSITIONS

Preferably, the laundry composition is a powder or particulate.

The term “particulate laundry detergent” in the context of this invention denotes free-flowing or compacted solid forms such as powders, granules, pellets, flakes, bars, briquettes or tablets and which are intended for and capable of wetting and cleaning domestic laundry such as clothing, linens and other household textiles. The term “linen” is often used to describe certain types of laundry items including bed sheets, pillow cases, towels, tablecloths, table napkins and uniforms. Textiles can include woven fabrics, non-woven fabrics, and knitted fabrics; and can include natural or synthetic fibres such as silk fibres, linen fibres, cotton fibres, polyester fibres, polyamide fibres such as nylon, acrylic fibres, acetate fibres, and blends thereof including cotton and polyester blends.

Examples of laundry detergents include heavy-duty detergents for use in the wash cycle of automatic washing machines, as well as fine wash and colour care detergents such as those suitable for washing delicate garments (e.g. those made of silk or wool) either by hand or in the wash cycle of automatic washing machines.

One preferred form for the composition according to the invention is a free-flowing powdered solid, with a loose (unpackaged) bulk density generally ranging from about 200g/l to about 1,300 g/l, preferably from about 400 g/l to about 1,000 g/l, more preferably from about 500g/l to about 900 g/l.

The particulate composition of the invention comprises from 3 to 80%, preferably from 10 to 60%, and more preferably from 15 to 50% (by weight based on the total weight of the composition) of one or more detersive surfactants selected from non-soap anionic surfactants, nonionic surfactants and mixtures thereof.

The term “detersive surfactant” in the context of particulate detergent formulations denotes a surfactant which provides a detersive (i.e. cleaning) effect to laundry treated as part of a domestic laundering process.

In addition to the sulphated ethoxylated $C_{10}$ Guerbet alcohol surfactant as described above, other non-soap anionic surfactants for use in particulate compositions are typically salts of organic sulfates and sulfonates 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 such materials include alkyl sulfates, alkyl ether sulfates, alkaryl sulfonates, alpha-olefin sulfonates and

mixtures thereof. The alkyl radicals preferably contain from 10 to 18 carbon atoms and may be unsaturated. The alkyl ether sulfates may contain from one to ten ethylene oxide or propylene oxide units per molecule, and preferably contain one to three ethylene oxide units per molecule. The counterion for anionic surfactants is generally an alkali metal such as sodium or potassium; or an ammoniacal counterion such as monoethanolamine, (MEA) diethanolamine (DEA) or triethanolamine (TEA). Mixtures of such counterions may also be employed.

Previously, a preferred class of non-soap anionic surfactant for use in particulate compositions includes alkylbenzene sulfonates, particularly linear alkylbenzene sulfonates (LAS) with an alkyl chain length of from 10 to 18 carbon atoms. Commercial LAS is a mixture of closely related isomers and homologues alkyl chain homologues, each containing an aromatic ring sulfonated at the "*para*" position and attached to a linear alkyl chain at any position except the terminal carbons. The linear alkyl chain typically has a chain length of from 11 to 15 carbon atoms, with the predominant materials having a chain length of about C12. Each alkyl chain homologue consists of a mixture of all the possible sulfophenyl isomers except for the 1-phenyl isomer. LAS is normally formulated into compositions in acid (i.e. HLAS) form and then at least partially neutralized in-situ.

Particulate compositions according to the invention may contain some alkyl benzene sulphonate in addition to the sulphated ethoxylated $C_{10}$ Guerbet alcohol surfactant as described above but it is preferred that the composition comprises less than 5% wt. more preferably less than 1% wt. and most preferably less than 0.1% wt. alkyl benzene sulphonate surfactant.

Mixtures of any of the above described materials may also be used.

In a typical particulate composition, the total level of non-soap anionic surfactant may suitably range from 5 to 25% (by weight based on the total weight of the composition).

Non-ionic surfactants may provide enhanced performance for removing very hydrophobic oily soil and for cleaning hydrophobic polyester and polyester/cotton blend fabrics.

Nonionic surfactants for use in particulate compositions are typically polyoxyalkylene compounds, i.e. the reaction product of alkylene oxides (such as ethylene oxide or propylene oxide or mixtures thereof) with starter molecules having a hydrophobic group and a reactive hydrogen atom which is reactive with the alkylene oxide. Such starter molecules include alcohols, acids, amides or alkyl phenols. Where the starter molecule is an alcohol, the reaction product is known as an alcohol alkoxylate. The polyoxyalkylene compounds can have a variety of block and heteric (random)

structures. For example, they can comprise a single block of alkylene oxide, or they can be diblock alkoxylates or triblock alkoxylates. Within the block structures, the blocks can be all ethylene oxide or all propylene oxide, or the blocks can contain a heteric mixture of alkylene oxides. Examples of such materials include $C_8$ to $C_{22}$ alkyl phenol ethoxylates with an average of from 5 to 25 moles of ethylene oxide per mole of alkyl phenol; and aliphatic alcohol ethoxylates such as $C_8$ to $C_{18}$ primary or secondary linear or branched alcohol ethoxylates with an average of from 2 to 40 moles of ethylene oxide per mole of alcohol.

A preferred class of nonionic surfactant for use in particulate comositions includes aliphatic $C_8$ to $C_{18}$, more preferably $C_{12}$ to $C_{15}$ primary linear alcohol ethoxylates with an average of from 3 to 20, more preferably from 5 to 10 moles of ethylene oxide per mole of alcohol.

Mixtures of any of the above described materials may also be used.

In particulate compositions the total level of non-ionic surfactant may suitably range from 1 to 10% (by weight based on the total weight of the composition).

Examples of suitable mixtures of non-soap anionic and/or nonionic surfactants for use in particulate comositions include mixtures of linear alkylbenzene sulfonate (preferably $C_{11}$ to $C_{15}$ linear alkyl benzene sulfonate) if present with sulphated ethoxylated $C_{10}$ Guerbet alcohol surfactant as described above, with sodium lauryl ether sulfate (preferably $C_{10}$ to $C_{18}$ alkyl sulfate ethoxylated with an average of 1 to 3 EO) and/or ethoxylated aliphatic alcohol (preferably $C_{12}$ to $C_{15}$ primary linear alcohol ethoxylate with an average of from 5 to 10 moles of ethylene oxide per mole of alcohol).

A particulate composition may also contain one or more cosurfactants (such as amphoteric (zwitterionic) and/or cationic surfactants) in addition to the non-soap anionic and/or nonionic detersive surfactants described above.

Specific cationic surfactants include $C_8$ to $C_{18}$ alkyl dimethyl ammonium halides and derivatives thereof in which one or two hydroxyethyl groups replace one or two of the methyl groups, and mixtures thereof. Cationic surfactant, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

Specific amphoteric (zwitterionic) surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinates, alkyl carboxyglycinates, alkyl amphoacetates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl

hydroxysultaines, acyl taurates and acyl glutamates, 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. Amphoteric (zwitterionic) surfactant, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

Preferably, a particulate composition may also include one or more builders. Builders are principally used to reduce water hardness. This is done either by sequestration or chelation (holding hardness minerals in solution), by precipitation (forming an insoluble substance), or by ion exchange (trading electrically charged particles). Builders can also supply and maintain alkalinity, which assists cleaning, especially of acid soils; help keep removed soil from redepositing during washing; and emulsify oily and greasy soils.

Builders for use in particulate compositions can be of the organic or inorganic type, or a mixture thereof. Non-phosphate builders are preferred.

Inorganic, non-phosphate builders for use in particulate compositions include carbonates, silicates, zeolites, and mixtures thereof.

Suitable carbonate builders for use in particulate compositions include mixed or separate, anhydrous or partially hydrated alkali metal carbonates, bicarbonates or sesquicarbonates. Preferably the alkali metal is sodium and/or potassium, with sodium carbonate being particularly preferred.

Suitable silicate builders include amorphous forms and/or crystalline forms of alkali metal (such as sodium) silicates. Preferred are crystalline layered sodium silicates (phyllosilicates) of the general formula (I)

$$NaMSi_xO_{2x+1}.yH_2O \qquad (I)$$

in which M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2 or 3 and y is a number from 0 to 20. Sodium disilicates of the above formula in which M is sodium and x is 2 are particularly preferred. Such materials can be prepared with different crystal structures, referred to as α, β, γ and δ phases, with δ-sodium disilicate being most preferred.

Zeolites are naturally occurring or synthetic crystalline aluminosilicates composed of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedra, which share oxygen-bridging vertices and form cage-like structures in crystalline

form. The ratio between oxygen, aluminium and silicon is O:(Al + Si) = 2:1. The frameworks acquire their negative charge by substitution of some Si by Al. The negative charge is neutralised by cations and the frameworks are sufficiently open to contain, under normal conditions, mobile water molecules. Suitable zeolite builders for use in the invention may be defined by the general formula (II):

$$Na_x[(AlO_2)_x(SiO_2)_y]\cdot zH_2O \qquad (II)$$

in which x and y are integers of at least 6, the molar ratio of x to y is in the range from about 1 to about 0.5, and z is an integer of at least 5, preferably from about 7.5 to about 276, more preferably from about 10 to about 264.

Suitable organic, non-phosphate builders for use in particulate compositions include polycarboxylates, in acid and/or salt form. When utilized in salt form, alkali metal (e.g. sodium and potassium) or alkanolammonium salts are preferred. Specific examples of such materials include sodium and potassium citrates, sodium and potassium tartrates, the sodium and potassium salts of tartaric acid monosuccinate, the sodium and potassium salts of tartaric acid disuccinate, sodium and potassium ethylenediaminetetraacetates, sodium and potassium N(2-hydroxyethyl)-ethylenediamine triacetates, sodium and potassium nitrilotriacetates and sodium and potassium N-(2-hydroxyethyl)-nitrilodiacetates. Polymeric polycarboxylates may also be used, such as polymers of unsaturated monocarboxylic acids (e.g. acrylic, methacrylic, vinylacetic, and crotonic acids) and/or unsaturated dicarboxylic acids (e.g. maleic, fumaric, itaconic, mesaconic and citraconic acids and their anhydrides). Specific examples of such materials include polyacrylic acid, polymaleic acid, and copolymers of acrylic and maleic acid. The polymers may be in acid, salt or partially neutralised form and may suitably have a molecular weight (Mw) ranging from about 1,000 to 100,000, preferably from about 2,000 to about 85,000, and more preferably from about 2,500 to about 75,000.

Mixtures of any of the above described materials may also be used. Preferred builders for use in particulate compositions may be selected from zeolites (of the general formula (II) defined above), sodium carbonate, δ-sodium disilicate and mixtures thereof.

Preferably the level of phosphate builders in a particulate composition is less than 1% (by weight based on the total weight of the composition). The term “phosphate builder” denotes alkali metal, ammonium and alkanol ammonium salts of polyphosphate, orthophosphate, and/or metaphosphate (e.g. sodium tripolyphosphate).

Builder, when included, may be present in a total amount ranging from about 10 to about 80%, preferably from about 15 to 50% (by weight based on the total weight of the composition).

A particulate composition may also include one or more fillers to assist in providing the desired density and bulk to the composition. Suitable fillers for use in the invention may generally be selected from neutral salts with a solubility in water of at least 1 gram per 100 grams of water at 20° C; such as alkali metal, alkaline earth metal, ammonium or substituted ammonium chlorides, fluorides, acetates and sulfates and mixtures thereof. Preferred fillers for use in the invention include alkali metal (more preferably sodium and/or potassium) sulfates and chlorides and mixtures thereof, with sodium sulfate and/or sodium chloride being most preferred.

Filler, when included, may be present in a total amount ranging from about 1 to about 80%, preferably from about 5 to about 50% (by weight based on the total weight of the composition).

A composition of the invention may contain one or more fatty acids and/ or salts thereof. Suitable fatty acids in the context of this invention include aliphatic carboxylic acids of formula RCOOH, where R is a linear or branched alkyl or alkenyl chain containing from 6 to 24, more preferably 10 to 22, most preferably from 12 to 18 carbon atoms and 0 or 1 double bond. Preferred examples of such materials include saturated C12-18 fatty acids such as lauric acid, myristic acid, palmitic acid or stearic acid; and fatty acid mixtures in which 50 to 100% (by weight based on the total weight of the mixture) consists of saturated C12-18 fatty acids. Such mixtures may typically be derived from natural fats and/or optionally hydrogenated natural oils (such as coconut oil, palm kernel oil or tallow).

The fatty acids may be present in the form of their sodium, potassium or ammonium salts and/or in the form of soluble salts of organic bases, such as mono-, di- or triethanolamine.
Mixtures of any of the above described materials may also be used.

Fatty acids and/or their salts, when included, may be present in an amount ranging from about 0.25 to 5%, more preferably from 0.5 to 5%, most preferably from 0.75 to 4% (by weight based on the total weight of the composition).

For formula accounting purposes, in the formulation, fatty acids and/or their salts (as defined above) are not included in the level of surfactant or in the level of builder.

A particulate composition may also include one or more polymeric cleaning boosters. such as soil release polymers, anti-redeposition polymers, and mixtures thereof.

Soil release polymers adsorb onto a fabric surface assisting soil removal. Suitable soil release polymers for use in particulate compositions include co-polyesters of dicarboxylic acids (for example adipic acid, phthalic acid or terephthalic acid), diols (for example ethylene glycol or propylene glycol) and polydiols (for example polyethylene glycol or polypropylene glycol). An example of such a material has a midblock formed from propylene terephthalate repeat units and one or two end blocks of capped polyalkylene oxide, typically PEG 750 to 2000 with methyl end capping. The weight average molecular weight ($M_w$) of such materials generally ranges from about 1000 to about 20,000 and preferably ranges from about 1500 to about 10,000.

Mixtures of any of the above described materials may also be used.

When included, a composition of the invention will preferably comprise from 0.05 to 6%, more preferably from 0.1 to 5% (by weight based on the total weight of the composition) of one or more soil release polymer(s) such as, for example, the copolyesters which are described above.

Anti-redeposition polymers stabilise the soil in the wash solution thus preventing redeposition of the soil. Suitable anti-redeposition polymers for use in the invention include alkoxylated polyethyleneimines. Polyethyleneimines are materials composed of ethylene imine units - $CH_2CH_2NH$- and, where branched, the hydrogen on the nitrogen is replaced by another chain of ethylene imine units. Preferred alkoxylated polyethylenimines for use in the invention have a polyethyleneimine backbone of about 300 to about 10000 weight average molecular weight ($M_w$). The polyethyleneimine backbone may be linear or branched. It may be branched to the extent that it is a dendrimer. The alkoxylation may typically be ethoxylation or propoxylation, or a mixture of both. Where a nitrogen atom is alkoxylated, a preferred average degree of alkoxylation is from 10 to 50, preferably from 15 to 40 alkoxy groups per modification. A preferred material is ethoxylated polyethyleneimine, with an average degree of ethoxylation being from 10 to 40, preferably from 15 to 35 ethoxy groups per ethoxylated nitrogen atom in the polyethyleneimine backbone. Another type of suitable anti-redeposition polymer for use in the invention includes cellulose esters and ethers, for example sodium carboxymethyl cellulose.

Mixtures of any of the above described materials may also be used.

When included, a particulate composition of the invention will preferably comprise from 0.05 to 6%, more preferably from 0.1 to 5% (by weight based on the total weight of the composition) of one or more anti-redeposition polymers such as, for example, the alkoxylated polyethyleneimines and/or cellulose esters and ethers which are described above.

A particulate composition of the invention may also include an oxidising agent to facilitate removal of tough food stains and other organic stains by chemical oxidation. The oxidising agent may, for example oxidize polyphenolic compounds commonly found in coffee, tea, wine, and fruit stains. Oxidation by the oxidising agent may also aid in bleaching, whitening, and disinfecting fabrics, and may also provide additional washing machine cleanliness and odour prevention. Suitable oxidising agents for use in the invention include peroxy bleach compounds such as sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

When included, a particulate composition will preferably comprise from 5 to 35%, preferably from 8 to 20% (by weight based on the total weight of the composition) of one or more oxidising agents such as the peroxy bleach compounds which are described above.

A bleaching activator such as N,N,N',N'-tetraacetylethylenediamine (TAED) or sodium nonanoyloxybenzenesulfonate (NOBS) may be included in conjunction with the one or more oxidising agents to improve bleaching action at low wash temperatures.

A bleaching catalyst may also be included in addition to or instead of a bleach activator. Typical bleaching catalysts include complexes of heavy metal ions such as cobalt, copper, iron, manganese or combinations thereof; with organic ligands such as 1,4,7-triazacyclononane (TACN), 1,4,7-trimethyl-1,4,7-triazacyclononane ($Me_3$-TACN), 1,5,9-trimethyl-1,5,9-triazacyclononane, 1,5,9-triazacyclododecane, 1,4,7-triazacycloundecane, tris[2-(salicylideneamino)ethyl]amine or combinations thereof.

A particulate composition may also contain one or more chelating agents for transition metal ions. Such chelating agents may also have calcium and magnesium chelation capacity, but preferentially bind heavy metal ions such as iron, manganese and copper.

Such chelating agents may help to improve the stability of the composition and protect for example against transition metal catalyzed decomposition of certain ingredients.

Suitable transition metal ion chelating agents include phosphonates, in acid and/or salt form. When utilized in salt form, alkali metal (e.g. sodium and potassium) or alkanolammonium salts are preferred. Specific examples of such materials include aminotris(methylene phosphonic acid) (ATMP), 1-hydroxyethylidene diphosphonic acid (HEDP) and diethylenetriamine penta(methylene phosphonic acid (DTPMP) and their respective sodium or potassium salts. HEDP is preferred. Mixtures of any of the above described materials may also be used.

Transition metal ion chelating agents, when included, may be present in an amount ranging from about 0.1 to about 10%, preferably from about 0.1 to about 3% (by weight based on the total weight of the composition). Mixtures of any of the above described materials may also be used.

A particulate composition may also comprise an effective amount of one or more enzyme selected from the group comprising, pectate lyase, protease, amylase, cellulase, lipase, mannanase and mixtures thereof. The enzymes are preferably present with corresponding enzyme stabilizers.

A particulate composition may contain further optional ingredients to enhance performance and/or consumer acceptability. Examples of such ingredients include dye transfer inhibitors (e.g. polyvinylpyrrolidone), foam control agents, preservatives (e.g. bactericides), anti-shrinking agents, anti-wrinkle agents, antioxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, ironing aids, colorants, fluorescers, pearlisers and/or opacifiers, and shading dye. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally, these optional ingredients are included individually at an amount of up to 5% (by weight based on the total weight of the composition).

Packaging and dosing

A composition of the invention may be packaged as unit doses in polymeric film soluble in the wash water. Alternatively, a composition of the invention may be supplied in multidose plastics packs with a top or bottom closure. A dosing measure may be supplied with the pack either as a part of the cap or as an integrated system.

A method of laundering fabric using a composition of the invention will usually involve diluting the dose of detergent composition with water to obtain a wash liquor and washing fabrics with the wash liquor so formed. In automatic washing machines the dose of detergent composition is typically put into a dispenser and from there it is flushed into the machine by the water flowing into the machine, thereby forming the wash liquor. From 5 up to about 65 litres of water may be used to form the

wash liquor depending on the machine configuration. The dose of detergent composition may be adjusted accordingly to give appropriate wash liquor concentrations.

The dilution step preferably provides a wash liquor which comprises *inter alia* from about 3 to about 20 g/wash of detersive surfactants (as are further defined above). The wash liquor preferably has a pH of from above 7 to less than 13, preferably from above 7 to less than 10.5.

A subsequent aqueous rinse step and drying the laundry is preferred.

DISHWASH COMPOSITIONS

Dish means a hard surface as is intended to be cleaned using a hand dish-wash composition and includes dishes, glasses, pots, pans, baking dishes and flatware made from any material or combination of hard surface materials commonly used in the making of articles used for eating and/or cooking.

**Surfactants for dishwash compositions**

Surfactant (detergent active) is generally chosen from anionic and non-ionic detergent actives. The cleaning composition may further or alternatively comprise cationic, amphoteric and zwitterionic surfactants.

Suitable synthetic (non-soap) anionic surfactants are water-soluble salts of organic sulphuric acid mono-esters and sulphonic acids which have in the molecular structure a branched or straight chain alkyl group containing from 6 to 22 carbon atoms in the alkyl part.

Examples of such anionic surfactants are water soluble salts of alkyl benzene sulfonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms; (primary) long chain (e.g. 6-22 C-atoms) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil; secondary alkanesulfonates; and mixtures thereof.

Also suitable are the salts of alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil; fatty acid monoglyceride sulphates; sulphates of ethoxylated aliphatic alcohols containing 1-12 ethylenoxy groups; alkylphenol ethylenoxy-ether sulphates with from 1 to 8 ethylenoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali, and mixtures thereof.

Previously, the preferred water-soluble synthetic anionic surfactants are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of alkyl-benzenesulfonates and mixtures with olefinsulfonates and alkyl sulfates, and the fatty acid mono-glyceride sulfates.

Non-ionic surfactants tend to reduce the foam produced on use of the composition. Consumers frequently associate high foam with powerful cleaning so it may be desirable to avoid the use of non-ionic surfactant altogether. For compositions where this is not an issue a suitable class of non-ionic surfactants can be broadly described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive hydrogen atom. The length of the hydrophilic or polyoxyalkylene chain which is attached to any particular hydrophobic group can be readily adjusted to yield a compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of non-ionic surfactants with the right HLB. Particular examples include: the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol/ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols having C6-C15 alkyl groups with 5 to 25 moles of ethylene oxide per mole of alkylphenol; and condensates of the reaction product of ethylene-diamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80 percent of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000.

Other classes of non-ionic surfactants are: tertiary amine oxides of structure R1 R2R3N-O, where R1 is an alkyl group of 8 to 20 carbon atoms and R2 and R3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide; tertiary phosphine oxides of structure R1R2R3P-O, where R1 is an alkyl group of 8 to 20 carbon atoms and R2 and R3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide; dialkyl sulphoxides of structure R1R2S=O, where R1 is an alkyl group of from 10 to 18 carbon atoms and R2 is methyl or ethyl, for instance methyl-tetradecyl sulphoxide; fatty acid alkylolamides, such as the ethanol amides; alkylene oxide condensates of fatty acid alkylolamides; and alkyl mercaptans.
If non-ionic surfactant is to be employed the amount present in the cleaning compositions of the invention will generally be at least 0.1 wt. percent, preferably at least 0.5 wt. percent, more preferably at least 1.0 wt. percent, but not more than 20 wt. percent, preferably at most 10 wt. percent and more preferably not more than 5 wt. percent.

It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in the compositions.

Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulfonate and sodium N 2-hydroxy-dodecyl-N-methyltaurate.

Examples of suitable cationic surfactants can be found among quaternary ammonium salts having one or two alkyl or aralkyl groups of from 8 to 20 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethylammonium chloride.

A specific group of surfactants are the tertiary amines obtained by condensation of ethylene and/or propylene oxide with long chain aliphatic amines. The compounds behave like non-ionic surfactants in alkaline medium and like cationic surfactants in acid medium.

Examples of suitable zwitterionic surfactants can be found among derivatives of aliphatic quaternary ammonium, sulfonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance betaine and betaine derivatives such as alkyl betaine, in particular C12-C16 alkyl betaine, 3-(N,N-dimethyl-N-hexadecylammonium)-propane 1-sulfonate betaine, 3-(dodecylmethyl-sulfonium)-propane 1-sulfonate betaine, 3-(cetylmethyl-phosphonium)-propane-1-sulfonate betaine and N,N-dimethyl-N-dodecyl-glycine. Other well known betaines are the alkylamidopropyl betaines e.g. those wherein the alkylamido group is derived from coconut oil fatty acids.

Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks: 'Surface Active Agents' Vol.1, by Schwartz and Perry, Interscience 1949; 'Surface Active Agents' Vol.2 by Schwartz, Perry and Berch, Interscience 1958; the current edition of 'McCutcheon's Emulsifiers and Detergents' published by Manufacturing Confectioners Company; 'Tenside-Taschenbuch', H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

The total level of surfactant is preferably from 3 to 40% wt. of the composition and typically along with the sulphated Guerbet surfactant the ratio between the LAS and SLES is from 80:20 to 30:70. The preferred ratio between the SLES and the CAPB is from 4:1 to 7:1 and the ratio between the PAS and the SLES is from 1:1 to 2:1.

**Optional ingredients for dishwash compositions**

The composition may include optional ingredients, such as abrasive particles and additional ingredients which aid formulation properties, stability and cleaning performance.

Magnesium and/or sodium sulphate are desirably included from 0.5 to 5 wt. percent in order to ensure the desired rheological properties are achieved.

A preservative system is also desirable, for example a mixture of CIT and MIT. BIT may also be used. The level of preservative will vary according to the expected storage temperature and the quality of raw materials. From 0.0001 to 0.1 wt percent is typical.

Sodium EDTA chelant is advantageously included in the compositions at a level of 0.01 to 0.5 wt percent. DMDMH (glydant) may also be included into the compositions at level of from 0.005 to 1 wt percent.

When the composition contains one or more anionic surfactants, the composition may preferably comprise detergent builders in an amount of more preferably from 0.1 to 25 weight percent. Suitable inorganic and organic builders are well known to those skilled in the art. Citric acid is a preferred buffer/ builder and may suitably be included at a level of from 0.01 to 0.5 wt percent.

The composition may also comprise ingredients such as colorants, whiteners, optical brighteners, soil suspending agents, detersive enzymes, compatible bleaching agents (particularly peroxide compounds and active chlorine releasing compounds), solvents, co-solvents, gel-control agents, freeze-thaw stabilisers, bactericides, preservatives, hydrotropes, polymers and perfumes.

Examples of optional enzymes include lipase, cellulase, protease, mannanase, and pectate lyase.

**Viscosity for dishwash compositions**

The liquid composition according to the invention preferably has a viscosity from 100 to 10,000 mPa.s, more preferably from 200 to 8,000 mPa.s, even more preferably from 400 to 6,500 mPa.s, and still even more preferably from 800 to 5,000 mPa.s, as measured at a shear rate of 20 $s^{-1}$ and at a temperature of 25 degrees Celsius.

**Packaging for dishwash compositions**

The liquid compositions may be packaged in any suitable form of container. Preferably the composition is packaged in a plastic bottle with a detachable closure /pouring spout. The bottle may

be rigid or deformable. A deformable bottle allows the bottle to be squeezed to aid dispensing. If clear bottles are used they may be formed from PET. Polyethylene or clarified polypropylene may be used. Preferably the container is clear enough that the liquid, with any visual cues therein, is visible from the outside. The bottle may be provided with one or more labels, or with a shrink wrap sleeve which is desirably at least partially transparent, for example 50 percent of the area of the sleeve is transparent. The adhesive used for any transparent label should preferably not adversely affect the transparency.

## EXAMPLES

Below is a laundry liquid formulation which comprises LAS obtained from plastic feedstock comprising 5% wt. of the total LAS present.

| Ingredient | Weight% |
|---|---|
| Linear alkyl benzene sulfonate acid | 8.2 |
| Alcohol ethoxylate | 6.2 |
| Sodium lauryl ether sulfate with 3 moles of EO | 6.2 |
| Monoethanolamine | 3.5 |
| Citric acid | 2 |
| Sodium benzoate | 1.0 |
| Potassium sulfite | 0.2 |
| Ethoxylate polyethylene imine | 1.2 |
| Polyester soil release polymer | 0.4 |
| Dequest 2010 | 0.5 |
| perfume | 1.3 |
| fluorescer | 0.2 |
| remainder | water |

Below are two unit dose laundry liquid formulations which comprises LAS obtained from plastic feedstock comprising 5% wt. of the total LAS present.

| Ingredient | Weight % | |
|---|---|---|
| Alcohol ethoxylate | 20.0 | 26.9 |
| Glycerol | 14.2 | 16.3 |
| Fatty Acid | 13.9 | 6.9 |
| LAS | 13.8 | 13.8 |
| Mono propylene glycol | 11.6 | 11.6 |
| Monoethanolamine | 6.9 | 4.9 |
| enzymes | 5.2 | 5.2 |
| perfume | 4.4 | 4.4 |
| Polyester cleaning polymer | 4.3 | 4.3 |
| Dequest 2066 | 2.8 | 2.8 |
| cleaning polymer | 2.0 | 2.0 |
| potassium sulphite | 0.4 | 0.4 |
| TinoPal CBS-CL | 0.3 | 0.3 |
| water | 0.2 | 0.2 |

In table 2 below are provided 2 different spray-dried solid laundry detergent composition (Ex 1 and Ex 2) according to the present invention were prepared having LAS obtained from plastic waste feedstock at an amount which constituted 5 wt.% of the total LAS present.

**Table 2: Spray-dried solid laundry composition**

| | Ex 1 | Ex 2 |
|---|---|---|
| Na LAS | 15 | 19 |
| PAS | 0 | 0 |
| SLES | 0 | 1 |
| Sodium carbonate | 13 | 14 |
| Sodium silicate | 7.0 | 10 |
| Layering agent (calcite) | 6.5 | 4.5 |
| Visual cues | 0.5 | 0.5 |
| Moisture | 2.19 | 2.5 |
| Perfume | 0.36 | 0.4 |
| Carboxylate polymer | 0.50 | 0.5 |
| Antiredeposition agent | 0 | 0.2 |
| Antifoam | 2 | 2 |
| Shading dye | 0 | 1.1 |
| Optical brightener (Tinopal) | 0.2 | 0 |
| Enzyme (protease, amylase, lipase, mannanase) | 0.2 | 0.5 |
| NDOM | 0.5 | 0.5 |
| Water | 2.0 | 2.6 |
| Sodium sulphate | Upto 100 | Upto 100 |

**EXAMPLE 2**

We conducted a GC trace for a fragrance comprising PRMS 1 and 2 and to compare the availability in the headspace the data shown below is for the area under the curve for waste-plastic feedstock derived LAS (A) divided by the area under the curve achieved for petroleum derived LAS (B).

A figure above 1 shows that more PRM is available in the headspace while a number below 1 means that moving from petroleum derived to waste plastic derived results in more PRM in the formulation and less in the headspace. Since the values are relative, it is concluded that the presence of PRMs 1 and 2 results in a change in availability in the presence of LAS derived from waste-plastic feedstock.

| Fragrance | *area% A/B* |
|---|---|
| Butanoic acid, 2-methyl-, 1-methylethyl ester | 0.6 |
| Beta myrcene | 0.8 |
| Octanal | 0.9 |
| 7-Octen-2-ol, 2,6-dimethyl- | 1.2 |
| Decanal | 0.8 |
| Linalool | 1.3 |
| 4-tert-Butylcyclohexyl acetate | 1.2 |
| Undecanal | 0.9 |
| 4-tert-Butylcyclohexyl acetate | 1.2 |
| Undecanal, 2-methyl- | 0.8 |
| 4-tert-Butylcyclohexyl acetate | 1.8 |
| 3-Cyclohexene-1-methanol, alpha,alpha,4-trimethyl-, 1-acetate | 1.2 |
| D-Limonene | 1.2 |
| Citronellol | 1.3 |
| Tricyclo[4.2.1.1(2,5)]dec-3-en-9-ol acetate stereoisomer | 1.2 |

## CLAIMS

1. A detergent composition comprising linear alkyl benzene sulphonate (LAS) obtained from waste plastic feedstock, and a fragrance comprising a first perfume raw material (PRM1) selected from aldehydes and a second perfume raw material (PRM2) selected from linalool; verdox; limonene; citronellol; 3-cyclohexene-1-methanol, alpha, alpha, 4-trimethyl-, 1-acetate; tricyclo[4.2.1.1(2,5)]dec-3-en-9-ol acetate stereoisomer; and mixtures thereof, and wherein the LAS obtained from waste plastic feedstock comprises a benzene moiety obtained from waste plastic feedstock and an alkyl obtained from petroleum feedstock or plant-based feedstock.

2. A detergent composition according to claim 1 wherein PRM1 is selected from octanal, undecanal; 2-methyl undecanal; beta-myrcene; butanoic acid; 2-methyl-, 1-methylethyler ether.

3. A detergent composition according to claim 1 or 2 comprising from 1 to 40% LAS.

4. A detergent according to any preceding claim comprising AES and/or AE.

5. A detergent composition according to any preceding claim wherein the LAS obtained from waste plastic feedstock comprises alkyl chains with an average chain length from 8 to 14 carbons.

6. A detergent composition according to any preceding claim wherein at least 30% wt. of the LAS obtained from waste plastic feedstock comprises alkyl chains with 12 carbons.

7. A detergent composition according to any preceding claim wherein from 1 to 30% wt. of the LAS obtained from waste plastic feedstock comprises 2-phenyl isomer.

8. A detergent composition according to any preceding claim which is a liquid detergent composition, a liquid dishwash composition or a powder laundry detergent composition.

9. A detergent composition according to any preceding claim comprising octahydro-2',3',8',8'-tetramethyl-(2')-acetonaphthone and/or octahydro-2',3',8',8'-tetramethyl-(3')-acetonaphthone (OTNE).

10. A detergent composition according to any preceding claim comprising verdyl acetate.

11. A detergent composition according to any preceding claim comprising dihydromyrcenol.

12. A detergent composition according to any preceding claim contained in a moulded article which comprises from 1 to 100% wt. PCR.

13. A detergent composition according to any preceding claim contained within a water-soluble capsule.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/073163

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D1/22 C11D1/24 C11D3/50 C11D17/04
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. |
|---|---|---|
| X,P | WO 2023/057532 A2 (UNILEVER IP HOLDINGS B V [NL]; UNILEVER GLOBAL IP LTD [GB] ET AL.) 13 April 2023 (2023-04-13) page 12, line 18 - line 27; claims 1, 9, 10 | 1-13 |
| A | US 2021/108154 A1 (SCHEIBEL JEFFREY JOHN [US] ET AL) 15 April 2021 (2021-04-15) paragraphs [0046], [0048], [0049], [0068]; claim 14; example 2; tables 1-2 | 1-13 |
| A | US 2009/081755 A1 (SCHMIEDEL PETER [DE] ET AL) 26 March 2009 (2009-03-26) examples 1, 3 | 1-13 |
| A | US 2017/022458 A1 (TRUJILLO RAFAEL [US] ET AL) 26 January 2017 (2017-01-26) examples 2, 18-43; tables 1-3 | 1-13 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 24 November 2023 | 05/12/2023 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Loiselet-Taisne, S |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/073163

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO 2023057532 A2 | 13-04-2023 | NONE | |
| US 2021108154 A1 | 15-04-2021 | CA 2993441 A1 | 16-02-2017 |
| | | CN 107922853 A | 17-04-2018 |
| | | EP 3334804 A1 | 20-06-2018 |
| | | JP 6755937 B2 | 16-09-2020 |
| | | JP 2018528300 A | 27-09-2018 |
| | | US 2017044465 A1 | 16-02-2017 |
| | | US 2019241838 A1 | 08-08-2019 |
| | | US 2021108154 A1 | 15-04-2021 |
| | | WO 2017027271 A1 | 16-02-2017 |
| | | ZA 201800390 B | 25-09-2019 |
| US 2009081755 A1 | 26-03-2009 | DE 102005054565 A1 | 16-05-2007 |
| | | EP 1948773 A1 | 30-07-2008 |
| | | ES 2572178 T3 | 30-05-2016 |
| | | JP 2009516034 A | 16-04-2009 |
| | | US 2009081755 A1 | 26-03-2009 |
| | | WO 2007054177 A1 | 18-05-2007 |
| US 2017022458 A1 | 26-01-2017 | CA 2991992 A1 | 26-01-2017 |
| | | EP 3325598 A1 | 30-05-2018 |
| | | JP 2018528993 A | 04-10-2018 |
| | | US 2017022458 A1 | 26-01-2017 |
| | | WO 2017015315 A1 | 26-01-2017 |