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(54) **LIQUID LAUNDRY DETERGENT COMPOSITION**

(57) The invention relates to a liquid laundry detergent composition comprising:
(i) from 50 to 80 wt.% of a linear alkyl benzene sulfonic acid surfactant; (ii) from 15 to 45 wt.% of an alkyl ether carboxylic acid surfactant of the following structure: R_1-$(OCH_2CH_2)_n$-OCH_2-COOH, wherein: R_1 is selected from saturated C_{16} to C_{22} linear or branched alkyl chains, and wherein n is selected from 10 to 24; (iii) less than 10 wt.% water; and (iv) from 0 to 20 wt.% non-ionic surfactant of the following structure: R_2-$(OCH_2CH_2)_n$-OH, wherein: R_2 is selected from saturated C_{12} to C_{22} linear or branched alkyl chains, and wherein n is selected from 5 to 30; and wherein the pH of the formulation is from 0.3 to 2.0.

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Description

FIELD OF INVENTION

[0001] The present invention provides a liquid laundry detergent composition. In particular, it relates to a concentrated liquid laundry detergent composition for use in domestic laundry.

BACKGROUND OF THE INVENTION

[0002] Laundry liquid formulations containing saturated long chain alkyl ether carboxylates with high degrees of ethoxylation are desirable as they provide enhanced cleaning particularly of sebum soil.

[0003] Saturated long chain alkyl ether carboxylates with high degrees of ethoxylation are solid waxy materials at room temperature.

[0004] To reduce weight in transportation it is desirable to have highly concentrated liquid laundry detergent with minimal contents of water. This may be used directly for washing or further mixed with other ingredients before washing. However it is highly desirable that the concentrated liquid detergent is a pourable liquid, both for ease of use for the consumer when using the concentrated liquid detergent, or when the concentrated liquid detergent is further processed into a more complex liquid detergent.

[0005] Accordingly, there is need for highly concentrated laundry detergents containing high levels of saturated long chain alkyl ether carboxylates that are pourable liquids at room temperature.

[0006] WO 2013/087286 (Unilever) discloses aqueous liquids formulations containing alkyl ether carboxylic acids, betaines, anionic surfactant, non-ionic surfactant for providing softening benefits.

[0007] WO 2014/060235 (Unilever) discloses an aqueous laundry detergent composition comprising (a) nonionic surfactant, (b) anionic surfactant, (c) alkyl ether carboxylic acid or carboxylate salt thereof, and, (d) a polyglucosamine or a copolymer of glucosamine and N-acetylglucosamine; and to its use to soften fabrics.

SUMMARY OF THE INVENTION

[0008] In one aspect, the present invention provides a liquid laundry detergent composition comprising:

(i) from 50 to 80 wt.% of a linear alkyl benzene sulfonic acid surfactant;
(ii) from 15 to 45 wt.% of an alkyl ether carboxylic acid surfactant of the following structure:

$$R_1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH,$$

wherein: R_1 is selected from saturated C_{16} to C_{22} linear or branched alkyl chains, preferably C_{16} to C_{18} linear alkyl chains, and wherein n is selected from 10 to 24;
(iii) less than 10 wt.% water;
(iv) from 0 to 20 wt.% non-ionic surfactant of the following structure

$$R_2\text{-}(OCH_2CH_2)_n\text{-}OH,$$

wherein: R_2 is selected from saturated C_{12} to C_{22} linear or branched alkyl chains, preferably C_{16} to C_{18} linear alkyl chains, and wherein n is selected from 5 to 30, preferably 10 to 20;

wherein the pH of the formulation is from 0.3 to 2.0.

[0009] Preferably the pH of the formulation is from 0.5 to 2.0, more preferably from 0.5 to 1.5.

[0010] A preferred liquid laundry detergent composition comprises:

(i) from 60 to 80 wt.% of a linear alkyl benzene sulfonic acid surfactant;
(ii) from 20 to 40 wt.% of an alkyl ether carboxylic acid surfactant of the following structure:

$$R_1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH,$$

wherein: R_1 is selected from saturated C_{16} to C_{18} linear alkyl chains,
and wherein n is selected from 10 to 20;

(iii) less than 10 wt.% water;
(iv) from 0 to 20 wt.% non-ionic surfactant of the following structure

$$R_2\text{-}(OCH_2CH_2)_n\text{-}OH,$$

wherein: R_2 is selected from saturated C_{12} to C_{22} linear or branched alkyl chains, preferably C_{16} to C_{18} linear alkyl chains, and wherein n is selected from 10 to 20;

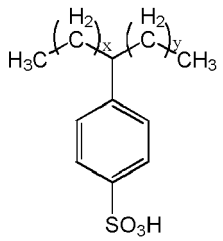
wherein the pH of the formulation is from 0.5 to 2.0;
and wherein the weight ratio of linear alkyl benzene sulfonic acid surfactant to the alkyl ether carboxylic acid surfactant is from 1.5:1 to 4:1.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Water contents are measured by Karl Fischer Titration. This may be accomplished using an automated Karl Fischer titrators, available from MetroOhm, and Mettler Toledo.
[0012] The pH of the formulation is that of a 1 wt.% solution of the liquid laundry detergent composition dissolved in demineralised water at 293K.
[0013] Room temperature as used herein is defined as 293K.

Linear alkyl benzene sulfonic acid surfactant

[0014] The liquid laundry composition comprises from 50 to 80 wt.%, preferably from 55 to 80 wt.%, more preferably from 55 to 75 wt.%, most preferably from 60 to 75 wt.% of the linear alkyl benzene sulfonic acid surfactant. Weights are expressed as the protonated form (i.e. the linear alkyl benzene anionic sulfonic acid form).
[0015] They may be used as salt version, for example alkali metal salt (preferably sodium salt), triethanolamine, monoethanol amine salt. The sodium salt is most preferred. Preferably the non-neutralised acid form is used.
[0016] Linear alkyl benzene sulfonic acid has the structure:



where x + y = 7, 8, 9 or 10.
Preferably x + y = 8 is present at a weight level greater than 28 wt.% of the total level of the linear alkyl benzene anionic surfactant.
Preferably x + y = 9 is present at greater than 28 wt.% of the total level of the linear alkyl benzene anionic surfactant. Weights are expressed as the protonated form.
[0017] The surfactant may be produced by a variety of different routes. Synthesis is discussed in Anionic Surfactants Organic Chemistry edited by H.W. Stache (Marcel Dekker, New York 1996).
[0018] Linear alkyl benzene sulfonic acid may be made by the sulfonation of linear alkyl benzene. The sulfation can be carried out with concentrated sulphuric acid, oleum or sulphur trioxide. Linear alkyl benzene sulfonic acid produced by reaction of linear alkyl benzene with sulphur trioxide is preferred.
[0019] Linear alkyl benzene may be produced by a variety of routes. Examples include: Benzene may be alkylated with n-alkenes using HF catalyst.
[0020] Benzene may be alkylated with n-alkenes in a fixed bed reactor with a solid acidic catalyst such as Alumosilicate (DETAL process).
[0021] Benzene may be alkylated with n-alkenes using an aluminium chloride catalyst. Benzene may be alkylated with n-chloroparaffins using an aluminium chloride catalyst.

Alkyl ether carboxylic acid

[0022] The liquid laundry composition comprises from 15 to 45 wt.%, preferably from 15 to 40 wt.%, more preferably

from 17.5 to 40 wt.%, most preferably from 20 to 40 wt.% of the alkyl ether carboxylic acid anionic surfactant.

[0023] Weights of alkyl ether carboxylic acid are calculated as the protonated form, R_2-$(OCH_2CH_2)_n$-OCH_2COOH, where n is from 10 to 24. They may be used as salt version for example sodium salt, triethanolamine, monoethanol amine salt. The sodium salt is most preferred.

[0024] n may be from 10 to 24, preferably from, 10 to 20, more preferably from 15 to 20.

[0025] Alkyl ether carboxylic acids synthesis is discussed in Anionic Surfactants Organic Chemistry edited by H.W. Stache (Marcel Dekker, New York 1996). They may be synthesised via the reaction of the corresponding alcohol ethoxylate with chloroacetic acid or monochloro sodium acetate in the presence of NaOH:-

$$R_2\text{-}(OCH_2CH_2)_n\text{-}OH + NaOH + ClCH_2COONa \rightarrow R_2\text{-}(OCH_2CH_2)_n\text{-}OCH_2COOH + NaCl + H_2O$$

[0026] In this synthesis residual R_2-$(OCH_2CH_2)_n$-OH may be present, preferably levels of R_2-$(OCH_2CH_2)_n$-OH are from 0 to 10 wt.% in the alkyl ether carboxylic acid. Low levels of diglycolic acid and glycolic acid may be present as bi products.

[0027] The alkyl ether carboxylic acid may also be synthesised via an oxidation reaction:-

$$R_2\text{-}(OCH_2CH_2)_n\text{-}O\ CH_2CH_2OH \rightarrow R_2\text{-}(OCH_2CH_2)_n\text{-}OCH_2COOH$$

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

[0028] The alkyl chain may be linear or branched, preferably it is linear.

[0029] The alkyl chain is preferably selected from $CH_3(CH_2)_{15}$ and $CH_3(CH_2)_{17}$

[0030] The alkyl ether carboxylic acid is most preferably of the structure:

$$CH_3(CH_2)_{17}(OCH_2CH_2)_{20}OCH_2COONa$$

[0031] Alkyl ether carboxylic acids are available from Kao (Akypo ®), Huntsman (Empicol®) and Clariant (Emulsogen ®).

[0032] The alkyl ether carboxylic acid is preferably used directly form the synthesis without further purification.

[0033] It is preferred that the weight ratio of linear alkyl benzene sulfonic acid surfactant to the alkyl ether carboxylic acid surfactant is preferably from 55:45 to 5:1, more preferably from 1.5:1 to 5:1. The weight ratio of linear alkyl benzene sulfonic acid surfactant to the alkyl ether carboxylic acid surfactant may be from 1.5:1 to 4.5:1, for example from 1.5:1 to 4:1; or from 2:1 to 4.5:1; or 2:1 to 4:1; or even 2.5:1 to 4.25:1; or even 2.5:1 to 4:1.

[0034] Water may be absent from the formulation, or present at a level of less than 10 wt.%, preferably less than 9 wt.%. If water is present, then it is present preferably at a level of from 0.01 to 8 wt.%, more preferably from 0.1 to 8 wt.%, most preferably from 1 to 8 wt.%.

[0035] Non-ionic surfactant may be absent from the formulation, or present at a level of less than 20 wt.%, preferably less than 15 wt.%, more preferably less than 12 wt.%. If non-ionic surfactant is present, then it is present preferably at a level of from 0.1 to 20 wt.%, more preferably from 0.1 to 15 wt.%, most preferably from 0.25 to 12 wt.%.

[0036] The non-ionic surfactant has the following structure:

$$R_2\text{-}(OCH_2CH_2)_n\text{-}OH,$$

wherein: R_2 is selected from saturated C_{12} to C_{22} linear or branched alkyl chains, preferably C_{16} to C_{18} linear alkyl chains, and wherein n is selected from 5 to 30, preferably 10 to 20.

[0037] The liquid detergent composition of the invention can be considered a concentrated liquid detergent composition. It may be used directly, or more preferably used as an ingredient to formulate further liquid detergent compositions.

[0038] Such further liquid detergent compositions may comprise further ingredients such as: fatty acids or salts thereof, shading dyes, enzymes (such as lipase, protease, amylase, cellulase), antiredeposition polymers, dye transfer inhibiting polymers, builders, structurants or thickening polymers, sequestrants, perfumes, and/or soil release polymers.

Experimental

[0039] The following mixtures containing 20 wt.% of alkyl ether carboxylate (R_1 = stearyl, n = 20, used as Na salt) and 80 wt.% second surfactant were prepared at 333K. At this temperature, all ingredients were liquid. They were then cooled to 293K. The phase results are shown in the table.

Second surfactant	Phase at 293K
linear alkyl benzene anionic sulfonic acid *inventive*	Pourable Liquid
Sodium lauryl ether sulfonate with 1 mole of ethoxylation *comparative*	Solid
Sodium lauryl ether sulfonate with 3 mole of ethoxylation *comparative*	Soft Gel
Non-ionic surfactant: alcohol ethoxylate with C13-15 and 7 moles of ethoxylation *comparative*	Soft Gel

[0040] The experiment with was repeated with different ratios of linear alkyl benzene anionic sulfonic acid to the alkyl ether carboxylate. The results are shown in the following table, along with the entry for the previous example:-

Wt% alkyl ether carboxylate	Wt% linear alkyl benzene anionic sulfonic acid	Phase at 293K
100 *comparative*	0	solid
50 *comparative*	50	Soft gel
40 *inventive*	60	Pourable Liquid
30 *inventive*	70	Pourable Liquid
20 *inventive*	80	Pourable Liquid

Claims

1. A liquid laundry detergent composition comprising:

(i) from 50 to 80 wt.% of a linear alkyl benzene sulfonic acid surfactant;
(ii) from 15 to 45 wt.% of an alkyl ether carboxylic acid surfactant of the following structure:

$$R_1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH,$$

wherein: R_1 is selected from saturated C_{16} to C_{22} linear or branched alkyl chains, preferably C_{16} to C_{18} linear alkyl chains, and wherein n is selected from 10 to 24;
(iii) less than 10 wt.% water;
(iv) from 0 to 20 wt.% non-ionic surfactant of the following structure

$$R_2\text{-}(OCH_2CH_2)_n\text{-}OH,$$

wherein: R_2 is selected from saturated C_{12} to C_{22} linear or branched alkyl chains, preferably C_{16} to C_{18} linear alkyl chains, and wherein n is selected from 5 to 30, preferably 10 to 20;

wherein the pH of the formulation is from 0.3 to 2.0.

2. A liquid laundry detergent composition according to claim 1, wherein the pH of the formulation is from 0.5 to 2.0, preferably from 0.5 to 1.5.

3. A liquid laundry detergent composition according to claim 1 or claim 2, wherein the non-ionic surfactant is present at a level of from 0.1 to 20 wt.%, preferably from 0.1 to 15 wt.%, more preferably from 0.25 to 12 wt.%.

4. A liquid laundry detergent composition according to any preceding claim, wherein the composition comprises from 55 to 80 wt.%, preferably from 55 to 75 wt.%, more preferably from 60 to 75 wt.% of the linear alkyl benzene sulfonic acid surfactant.

5. A liquid laundry detergent composition according to any preceding claim, wherein the composition comprises from 15 to 40 wt.%, preferably from 17.5 to 40 wt.%, more preferably from 20 to 35 wt.% of the alkyl ether carboxylic acid anionic surfactant.

6. A liquid laundry detergent composition according to any preceding claim, wherein the weight ratio of linear alkyl benzene sulfonic acid surfactant to the alkyl ether carboxylic acid surfactant is from 55:45 to 5:1, preferably from 1.5:1 to 5:1.

7. A liquid laundry detergent composition according to any preceding claim, wherein the level of water is from 0 to less than 9 wt.%, preferably from 0.01 to 8 wt.%, more preferably from 0.1 to 8 wt.%, most preferably from 1 to 8 wt.%.

8. A liquid laundry detergent composition according to claim 1, comprising:

(v) from 60 to 80 wt.% of a linear alkyl benzene sulfonic acid surfactant;
(vi) from 20 to 40 wt.% of an alkyl ether carboxylic acid surfactant of the following structure:

$$R_1\text{-}(OCH_2CH_2)_n\text{-}OCH_2\text{-}COOH,$$

wherein: R_1 is selected from saturated C_{16} to C_{18} linear alkyl chains,
and wherein n is selected from 15 to 20;

(vii) less than 10 wt.% water;
(viii) from 0 to 20 wt.% non-ionic surfactant of the following structure

$$R_2\text{-}(OCH_2CH_2)_n\text{-}OH,$$

wherein: R_2 is selected from saturated C_{12} to C_{22} linear or branched alkyl chains, preferably C_{16} to C_{18} linear alkyl chains, and wherein n is selected from 10 to 20;

wherein the pH of the formulation is from 0.5 to 2.0;
and wherein the weight ratio of linear alkyl benzene sulfonic acid surfactant to the alkyl ether carboxylic acid surfactant is from 1.5:1 to 4:1.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 17 0422

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	US 2015/252294 A1 (WEERASOORIYA UPALI P [US] ET AL) 10 September 2015 (2015-09-10) * paragraph [0007] * * paragraph [0033] - paragraph [0043] *	1-8	INV. C11D1/37 C11D1/83 ADD. C11D1/06 C11D1/22 C11D1/72
Y	EP 0 328 177 A2 (UNILEVER NV [NL]; UNILEVER PLC [GB]) 16 August 1989 (1989-08-16) * figures 2a,2b * * page 4, line 41 - line 49 *	1-8	
A	DE 10 2013 218614 A1 (HENKEL AG & CO KGAA [DE]) 19 March 2015 (2015-03-19) * paragraph [0042] * * page 10; example B; table 1 * * claim 1 *	1-8	
A	WO 2016/198263 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC D/B/A UNILEVER [US]) 15 December 2016 (2016-12-15) * page 8, line 1 - line 2 * * page 10, line 11 - line 13 * * claims 1,6 *	1-8	TECHNICAL FIELDS SEARCHED (IPC) C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	15 August 2017	Cetinkaya, Murat

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 17 17 0422

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15-08-2017

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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- WO 2013087286 A **[0006]**
- WO 2014060235 A **[0007]**
- DE 3135946 **[0027]**
- DE 2816127 **[0027]**
- EP 0304763 A **[0027]**

Non-patent literature cited in the description

- Anionic Surfactants Organic Chemistry. Marcel Dekker, 1996 **[0025]**