



(51) International Patent Classification:

C11D 1/83 (2006.01)

C11D 1/75 (2006.01)

C11D 3/30 (2006.01)

(21) International Application Number:

PCT/US2017/037816

(22) International Filing Date:

16 June 2017 (16.06.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16175143.3

17 June 2016 (17.06.2016)

EP

(71) Applicant: THE PROCTER & GAMBLE COMPANY

[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).

(72) Inventors: BRAECKMAN, Karl, Ghislain;

Brussels Innovation Centre, Temselaan 100, B-1853 Strombeek-Bever (BE). RODRIGUEZ RODRIGUEZ, Sergio; Brussels Innovation Centre, Temselaan 100, B-1853 Strombeek-Bever (BE). DELPLANCKE, Patrick, Firmin August; Brussels Innovation Centre, Temselaan 100, B-1853 Strombeek-Bever (BE). KEULEERS, Robby, Renilde François; Brussels Innovation Centre, Temselaan 100, B-1853 Strombeek-Bever (BE).

(74) Agent: KREBS, Jay A.; c/o THE PROCTER & GAMBLE

COMPANY, Global IP Services, One Procter & Gamble Plaza, C9, Cincinnati, Ohio 45202 (US).

(81) Designated States (unless otherwise indicated, for every

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

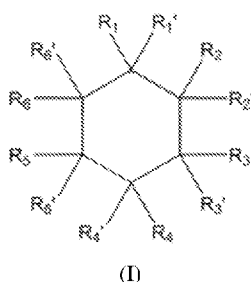
(84) Designated States (unless otherwise indicated, for every

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

Published:

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

(54) Title: LIQUID DETERGENT COMPOSITION



(57) **Abstract:** A hand dishwashing detergent composition comprising anionic surfactant and an amine oxide surfactant comprising a low-cut amine oxide of formula $RaRbRcAO$ wherein Ra and Rb are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein Rc is selected from C10 alkyls and mixtures thereof, and a cyclic diamine of Formula (I) wherein two of the Rs , are selected from the group consisting of NH_2 , (C1-C4) NH_2 and mixtures thereof and the remaining Rs are independently selected from H, linear or branched alkyl or alkenyl having from 1 to 10 carbon atoms.



LIQUID DETERGENT COMPOSITION

FIELD OF THE INVENTION

5 The present invention relates to a hand dishwashing detergent composition comprising anionic surfactant, low-cut amine oxide and a cyclic diamine. The composition provides improved cleaning and foaming properties and present good stability.

BACKGROUND OF THE INVENTION

10 Hand dishwashing detergent compositions should have a good suds profile while providing good soil and grease cleaning. However, a dichotomy exists between some cleaning technologies that are good for grease cleaning but impair on suds.

 Users usually see foam as an indicator of the performance of the detergent composition. Moreover, the user of a hand dishwashing detergent composition also uses the sudsing profile and the appearance of the foam (density, whiteness) as an indicator that the wash solution or cleaning
15 implement still contains active detergent ingredients. The user usually doses the dishwashing detergent depending on the foam ability and renews the wash solution when the suds subsides or when the foam does not look strong enough. Thus, a wash liquor comprising a dishwashing detergent composition that generates little foam would tend to be replaced by the user more
20 frequently than it is necessary. Hand dishwashing detergent compositions need to provide good grease cleaning and to exhibit good foam height and appearance as well as good foam generation during the initial mixing of the detergent with water and good lasting foam during the entire manual dishwashing operation.

 There is a need to provide hand dishwashing compositions with improved foam properties
25 while at the same time providing improved grease cleaning.

SUMMARY OF THE INVENTION

 According to a first aspect of the invention, there is provided a hand dishwashing detergent composition. The composition comprises anionic surfactant, amine oxide surfactant comprising a
30 low-cut amine oxide and a cyclic diamine.

 The composition preferably comprises from about 1 to about 15%, preferably from 1.5 to about 10%, more preferably from about 2 to about 8% by weight of the composition of amine oxide surfactant. The amine oxide surfactant can be a mixture of amine oxides comprising a low-cut amine oxide and a mid-cut amine oxide.

The low-cut amine oxide of the composition of the invention has the formula $RaRbRcAO$ wherein Ra and Rb are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein Rc is selected from C10 alkyls and mixtures thereof. The composition optionally comprises a mid-cut amine oxide of formula $RdReRfAO$ wherein Rd and Re are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein Rf is selected from C12-C16 alkyls and mixtures thereof.

Preferred cyclic diamines for use herein include 1,3-bis (aminomethyl) cyclohexane (1,3-BAC), 2-methylcyclohexane-1,3-diamine, 4-methylcyclohexane-1,3-diamine and mixtures thereof, preferably 2-methylcyclohexane-1,3-diamine, 4-methylcyclohexane-1,3-diamine and mixtures thereof. Compositions comprising 1,3-BAC, 2-methylcyclohexane-1,3-diamine, 4-methylcyclohexane-1,3-diamine and mixtures thereof, provide very good grease removal from dishware and the dishware does not feel slippery during rinse.

The composition of the invention provides good cleaning and good suds profile. It presents benefits in terms of tough food cleaning (cooked-, baked- and burnt-on soils) and grease cleaning.

When the composition of the invention is in use, the appearance of the suds is very appealing. The suds are constituted by airy bubbles that seem to travel very quickly from the cleaning implement to the items to be cleaned. This is believed to contribute to a faster and better cleaning.

In a preferred low-cut amine oxide for use herein Rc is n-decyl. In another preferred low-cut amine oxide for use herein Ra and Rb are both methyl. In an especially preferred low-cut amine oxide for use herein Ra and Rb are both methyl and Rc is n-decyl.

Preferably, the amine oxide comprises less than about 5%, more preferably less than 3% by weight of the amine oxide of an amine oxide of formula $RgRhRiAO$ wherein Rg and Rh are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein Ri is selected from C8 alkyls and mixtures thereof. Compositions comprising $RgRhRiAO$ tend to be instable and do not provide very suds mileage.

The composition of the invention comprises anionic surfactant, the anionic surfactant can be any anionic cleaning surfactant, preferably the anionic surfactant comprises a sulphate anionic surfactant, more preferably an alkyl sulphate and/or alkoxyated sulfate anionic surfactant, preferably an alkyl alkoxyated sulphate, preferably the alkoxyated anionic surfactant has an average alkoxylation degree of from about 0.2 to about 3, preferably from about 0.2 to about 2, most preferably from about 0.2 to about 1.0. Also preferred are branched anionic surfactants having a weight average level of branching of from about 5% to about 40%.

Preferably the composition of the invention comprises from about 1% to about 60%, preferably from about 5% to about 50%, more preferably from about 8% to about 40% by weight

of the composition of total surfactant. Preferably the composition of the invention comprises from about 5% to about 40% by weight of the composition of anionic surfactant, more preferably from about 8% to about 35%, yet more preferably from about 10% to about 30%.

Preferably the anionic surfactant and the amine oxide are in a weight ratio of from about 1:1 to about 10:1. Preferred anionic surfactant amine oxide weight ratio have been found to be from 2:1 to 5:1 and from 5:1 to 10:1. Compositions in which the anionic surfactant and the amine oxide surfactant are in these ratios present very good cleaning and suds mileage.

Preferably, the composition of the invention comprises less than about 2%, more preferably less than 1% by weight of the composition of non-ionic surfactants. It has been found that the compositions with this low level of non-ionic surfactant can provide a more robust cleaning system.

According to the second aspect of the invention, there is provided a process for making the dishwashing detergent of the invention comprising a low-cut and a mid-cut amine oxide. The process requires the use of two different streams one comprising the low-cut amine oxide and another comprising the mid-cut amine oxide.

For the purpose of this invention "dishware" herein includes cookware and tableware.

DETAILED DESCRIPTION OF THE INVENTION

The present invention envisages a hand dishwashing detergent composition. Preferably in liquid form. The detergent composition comprises a surfactant system comprising anionic surfactant and amine oxide surfactant and a cleaning amine. It provides very good cleaning, especially grease cleaning. It is also good for tough food cleaning, including cook-, baked- and burnt-on cleaning. It provides very good suds mileage and suds profile.

The detergent composition

The detergent composition is a hand dishwashing detergent, preferably in liquid form. It typically contains from 30% to 95%, preferably from 40% to 90%, more preferably from 50% to 85% by weight of the composition of a liquid carrier in which the other essential and optional components are dissolved, dispersed or suspended. One preferred component of the liquid carrier is water.

Preferably the pH of the composition is adjusted to be from between 6 and 10, more preferably between 6.5 and 9.5, even more preferably between 7 and 9, most preferably between 7.5 and 8.5. The pH is measured as a 10 wt% product solution in deionised water at 20°C. The pH of the composition can be adjusted using pH modifying ingredients known in the art.

The composition can comprises 1% to 60%, preferably from 5% to 50%, more preferably from 8% to 40% of total surfactant. In addition to the anionic and amine oxide surfactant the composition can optionally comprise non-ionic surfactant, zwitterionic and/or cationic surfactant.

5 Amine oxide surfactant

The amine oxide surfactant improves the cleaning and boosts the suds of the detergent composition. This improved cleaning and suds boosting is achieved by the combination of the anionic surfactant and amine oxide and the presence of low cut amine oxide surfactant at the claimed level.

10

Low-cut amine oxide

Within the meaning of the present invention “low-cut amine oxide” means an amine oxide in which at least 90%, preferably at least 95% and more preferably at least 98% and especially at least 100% of the cut has the formula: $R_aR_bR_cAO$ wherein R_a and R_b are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R_c is selected from C10 alkyls and mixtures thereof.

15

Mid-cut amine oxide

Within the meaning of the present invention “mid-cut amine oxide” means an amine oxide in which at least 90%, preferably at least 95% and more preferably at least 98% and especially at least 100% of the cut has the formula: $R_dR_eR_fAO$ wherein R_d and R_e are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R_f is selected from C12-C16 alkyls and mixtures thereof.

20

25 Anionic surfactant

Anionic surfactants include, but are not limited to, those surface-active compounds that contain an organic hydrophobic group containing generally 8 to 22 carbon atoms or generally 8 to 18 carbon atoms in their molecular structure and at least one water-solubilizing group preferably selected from sulfonate, sulfate, and carboxylate so as to form a water-soluble compound. Usually, the hydrophobic group will comprise a C 8-C 22 alkyl, or acyl group. Such surfactants are employed in the form of water-soluble salts and the salt-forming cation usually is selected from sodium, potassium, ammonium, magnesium and mono-, di- or tri-alkanolammonium, with the sodium, cation being the usual one chosen.

30

The anionic surfactant can be a single surfactant but usually it is a mixture of anionic surfactants. Preferably the anionic surfactant comprises a sulphate surfactant, more preferably a sulphate surfactant selected from the group consisting of alkyl sulphate, alkyl alkoxy sulphate and mixtures thereof. Preferred alkyl alkoxy sulphates for use herein are alkyl ethoxy sulphates.

5 Preferably the anionic surfactant is alkoxyated, more preferably, an alkoxyated branched anionic surfactant having an alkoxylation degree of from about 0.2 to about 4, even more preferably from about 0.3 to about 3, even more preferably from about 0.4 to about 1.5 and especially from about 0.4 to about 1. Preferably, the alkoxy group is ethoxy. When the branched anionic surfactant is a mixture of surfactants, the alkoxylation degree is the weight average
10 alkoxylation degree of all the components of the mixture (weight average alkoxylation degree). In the weight average alkoxylation degree calculation the weight of anionic surfactant components not having alkoxyated groups should also be included.

Weight average alkoxylation degree = $(x_1 * \text{alkoxylation degree of surfactant 1} + x_2 * \text{alkoxylation degree of surfactant 2} + \dots) / (x_1 + x_2 + \dots)$

15 wherein $x_1, x_2, \dots$ are the weights in grams of each anionic surfactant of the mixture and alkoxylation degree is the number of alkoxy groups in each anionic surfactant.

Preferably the anionic surfactant to be used in the detergent of the present invention is a branched anionic surfactant having a level of branching of from about 5% to about 40%, preferably from about 10 to about 35% and more preferably from about 20% to about 30%. Preferably, the
20 branching group is an alkyl. Typically, the alkyl is selected from methyl, ethyl, propyl, butyl, pentyl, cyclic alkyl groups and mixtures thereof. Single or multiple alkyl branches could be present on the main hydrocarbyl chain of the starting alcohol(s) used to produce the anionic surfactant used in the detergent of the invention. Most preferably the branched anionic surfactant is selected from alkyl sulphates, alkyl ethoxy sulphates, and mixtures thereof.

25 The branched anionic surfactant can be a single anionic surfactant or a mixture of anionic surfactants. In the case of a single surfactant the percentage of branching refers to the weight percentage of the hydrocarbyl chains that are branched in the original alcohol from which the surfactant is derived.

30 In the case of a surfactant mixture the percentage of branching is the weight average and it is defined according to the following formula:

Weight average of branching (%) = $[(x_1 * \text{wt\% branched alcohol 1 in alcohol 1} + x_2 * \text{wt\% branched alcohol 2 in alcohol 2} + \dots) / (x_1 + x_2 + \dots)] * 100$

wherein $x_1, x_2, \dots$ are the weight in grams of each alcohol in the total alcohol mixture of the alcohols which were used as starting material for the anionic surfactant for the detergent of the invention. In the weight average branching degree calculation the weight of anionic surfactant components not having branched groups should also be included.

5 Preferably, the anionic surfactant is a branched anionic surfactant having a level of branching of from about 5% to about 40%, preferably from about 10 to about 35% and more preferably from about 20% to about 30%, more preferably the branched anionic surfactant comprises more than 50% by weight thereof of an alkyl ethoxylated sulphate. Preferably the branched anionic surfactant has an average ethoxylation degree of from about 0.2 to about 3 and
10 preferably an average level of branching of from about 5% to about 40%.

Preferably, the anionic surfactant comprises at least 50%, more preferably at least 60% and preferably at least 70% by weight of the anionic surfactant, more preferably the branched anionic surfactant comprises more than 50% by weight thereof of an alkyl ethoxylated sulphate having an ethoxylation degree of from about 0.2 to about 3 and preferably a level of branching of from about
15 5% to about 40%.

Sulphate Surfactants

Suitable sulphate surfactants for use herein include water-soluble salts of C8-C18 alkyl or hydroxyalkyl, sulphate and/or ether sulfate. Suitable counterions include alkali metal cation or
20 ammonium or substituted ammonium, but preferably sodium.

The sulphate surfactants may be selected from C8-C18 primary, branched chain and random alkyl sulphates (AS); C8-C18 secondary (2,3) alkyl sulphates; C8-C18 alkyl alkoxy sulphates (AExS) wherein preferably x is from 1-30 in which the alkoxy group could be selected from ethoxy, propoxy, butoxy or even higher alkoxy groups and mixtures thereof.

25 Alkyl sulfates and alkyl alkoxy sulfates are commercially available with a variety of chain lengths, ethoxylation and branching degrees. Commercially available sulphates include, those based on Neodol alcohols ex the Shell company, Lial – Isalchem and Safol ex the Sasol company, natural alcohols ex The Procter & Gamble Chemicals company.

Preferably, the branched anionic surfactant comprises at least 50%, more preferably at least
30 60% and especially at least 70% of a sulphate surfactant by weight of the branched anionic surfactant. Especially preferred detergents from a cleaning view point are those in which the branched anionic surfactant comprises more than 50%, more preferably at least 60% and especially at least 70% by weight thereof of sulphate surfactant and the sulphate surfactant is selected from the group consisting of alkyl sulphate, alkyl ethoxy sulphates and mixtures thereof. Even more

preferred are those in which the branched anionic surfactant has a degree of ethoxylation of from about 0.2 to about 3, more preferably from about 0.3 to about 2, even more preferably from about 0.4 to about 1.5, and especially from about 0.4 to about 1 and even more preferably when the anionic surfactant has a level of branching of from about 10% to about 35%, %, more preferably from about 20% to 30%.

Sulphonate Surfactants

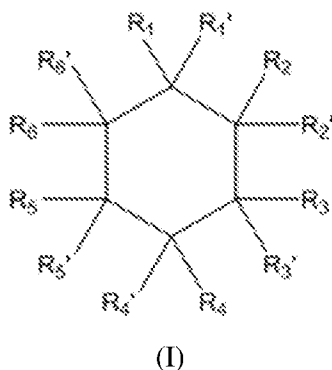
Suitable sulphonate surfactants for use herein include water-soluble salts of C8-C18 alkyl or hydroxyalkyl sulphonates; C11-C18 alkyl benzene sulphonates (LAS), modified alkylbenzene sulphonate (MLAS) as discussed in WO 99/05243, WO 99/05242, WO 99/05244, WO 99/05082, WO 99/05084, WO 99/05241, WO 99/07656, WO 00/23549, and WO 00/23548; methyl ester sulphonate (MES); and alpha-olefin sulphonate (AOS). Those also include the paraffin sulphonates may be monosulphonates and/or disulphonates, obtained by sulphonating paraffins of 10 to 20 carbon atoms. The sulfonate surfactant also include the alkyl glyceryl sulphonate surfactants.

Cyclic diamine

The composition of the invention preferably comprises from about 0.1% to about 10%, more preferably from about 0.2% to about 5%, and especially from about 0.3% to about 2%, by weight of the composition, of a cyclic diamine of Formula (I).

The term “cyclic diamine” herein encompasses a single cleaning amine and a mixture thereof. The amine can be subjected to protonation depending on the pH of the cleaning medium in which it is used.

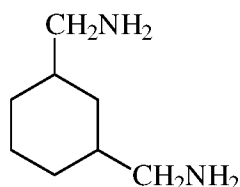
Cyclic diamine of Formula (I):



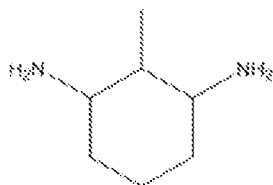
two of the substituents $R_s(R_1-R_6, R_1'-R_6')$ are independently selected from the group consisting of NH_2 , $(C1-C4)NH_2$ and mixtures thereof and the remaining substituents R_s are independently selected from H, linear or branched alkyl or alkenyl having from 1 to 10 carbon atoms.

The amine of Formula (I) is a cyclic amine with two primary amine functionalities. The primary amines can be in any position in the cycle but it has been found that in terms of grease cleaning, better performance can be obtained when the primary amines are in positions 1,3. It has also been found advantageous in terms of grease cleaning amines in which one of the substituents is $-CH_3$ and the rest are H.

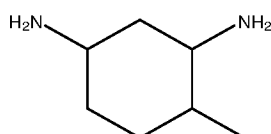
Preferred cyclic diamines for use herein are selected from the group consisting of:



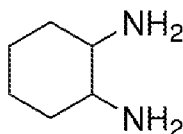
1, 3-bis(methylamine)-cyclohexane,



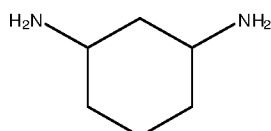
2-methylcyclohexane-1,4-diamine,



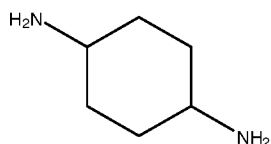
4-methylcyclohexane-1,4-diamine,



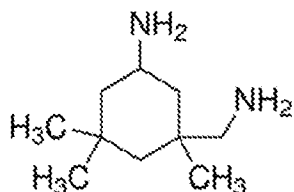
Cyclohexane-1,2-diamine



Cyclohexane-1,3-diamine,



Cyclohexane-1,4-diamine,



5 Isophorone diamine; and a mixture thereof.

Especially preferred for use herein are cyclic diamines selected from the group consisting of 1, 3-bis(methylamine)-cyclohexane, 2-methylcyclohexane-1,3-diamine, 4-methylcyclohexane-1,3-diamine and mixtures thereof. 1, 3-bis(methylamine)-cyclohexane is
 10 especially preferred for use herein. Mixtures of 2-methylcyclohexane-1,3-diamine, 4-methylcyclohexane-1,3-diamine are most preferred for use herein.

Nonionic surfactant, when present, is comprised in an amount of less than 2%, preferably less than 1% by weight of the composition. Suitable nonionic surfactants include the condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide. The alkyl chain of the
 15 aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 10 to 18 carbon atoms, preferably from 10 to 15 carbon atoms with from 2 to 18 moles, preferably 2 to 15, more preferably 5-12 of ethylene oxide per mole of alcohol. Highly preferred nonionic surfactants are the condensation products of guerbet alcohols with from
 20 2 to 18 moles, preferably 2 to 15, more preferably 5-12 of ethylene oxide per mole of alcohol.

Zwitterionic surfactant

Other suitable surfactants include betaines, such as alkyl betaines, alkylamidobetaine, amidazoliniumbetaine, sulfobetaine (INCI Sultaines) as well as the Phosphobetaine and preferably
 25 meets formula I:

$R^1-[CO-X (CH_2)_n]_x-N^+(R^2)(R_3)-(CH_2)_m-[CH(OH)-CH_2]_y-Y$ (I) wherein

R^1 is a saturated or unsaturated C6-22 alkyl residue, preferably C8-18 alkyl residue, in particular a saturated C10-16 alkyl residue, for example a saturated C12-14 alkyl residue;

X is NH, NR^4 with C1-4 Alkyl residue R^4 , O or S,

n a number from 1 to 10, preferably 2 to 5, in particular 3,

5 x 0 or 1, preferably 1,

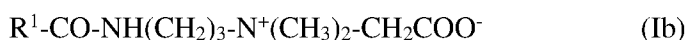
R^2 , R^3 are independently a C1-4 alkyl residue, potentially hydroxy substituted such as a hydroxyethyl, preferably a methyl.

m a number from 1 to 4, in particular 1, 2 or 3,

y 0 or 1 and

10 Y is COO, SO₃, OPO(OR⁵)O or P(O)(OR⁵)O, whereby R^5 is a hydrogen atom H or a C1-4 alkyl residue.

Preferred betaines are the alkyl betaines of the formula (Ia), the alkyl amido propyl betaine of the formula (Ib), the Sulfo betaines of the formula (Ic) and the Amido sulfobetaine of the formula (Id);



20 $R^1-CO-NH-(CH_2)_3-N^+(CH_3)_2-CH_2CH(OH)CH_2SO_3^-$ (Id) in which R^1 is the same meaning as in formula I. Particularly preferred betaines are the Carbobetaine [wherein $Y=COO^-$], in particular the Carbobetaine of the formula (Ia) and (Ib), more preferred are the Alkylamidobetaine of the formula (Ib).

Examples of suitable betaines and sulfobetaine are the following [designated in accordance with INCI]: Almondamidopropyl of betaines, Apricotamidopropyl betaines, Avocamidopropyl of betaines, Babassuamidopropyl of betaines, Behenamidopropyl betaines, Behenyl of betaines, betaines, Canolamidopropyl betaines, Capryl/Capram idopropyl betaines, Carnitine, Cetyl of betaines, Cocamidopropyl of betaines, Cocamidopropyl betaines, Cocamidopropyl Hydroxysultaine, Coco betaines, Coco Hydroxysultaine, Coco/Oleamidopropyl betaines, Coco Sultaine, Decyl of betaines, Dihydroxyethyl Oleyl Glycinate, Dihydroxyethyl Soy Glycinate, Dihydroxyethyl Stearyl Glycinate, Dihydroxyethyl Tallow Glycinate, Dimethicone Propyl of PG-betaines, Erucamidopropyl Hydroxysultaine, Hydrogenated Tallow of betaines, Isostearamidopropyl betaines, Lauramidopropyl betaines, Lauryl of betaines, Lauryl Hydroxysultaine, Lauryl Sultaine, Milkamidopropyl betaines, Minkamidopropyl of betaines, Myristamidopropyl

betaines, Myristyl of betaines, Oleam idopropyl betaines, Oleam idopropyl Hydroxysultaine, Oleyl of betaines, Olivamidopropyl of betaines, Palmam idopropyl betaines, Palm itam idopropyl betaines, Palmitoyl Carnitine, Palm Kernelam idopropyl betaines, Polytetrafluoroethylene Acetoxypopyl of betaines, Ricinoleam idopropyl betaines, Sesam idopropyl betaines, Soyam
5 idopropyl betaines, Stearam idopropyl betaines, Stearyl of betaines, Tallowam idopropyl betaines, Tallowam idopropyl Hydroxysultaine, Tallow of betaines, Tallow Dihydroxyethyl of betaines, Undecylenam idopropyl betaines and Wheat Germam idopropyl betaines.

A preferred betaine is, for example, Cocoamidopropylbetain.

10 The detergent composition herein may comprise a number of optional ingredients such as builders, chelants, conditioning polymers, cleaning polymers, surface modifying polymers, soil flocculating polymers, structurants, rheology modifiers, emmolients, humectants, skin rejuvenating actives, enzymes, carboxylic acids, scrubbing particles, bleach and bleach activators, perfumes, malodor control agents, pigments, dyes, opacifiers, beads, pearlescent particles,
15 microcapsules, organic solvents, hydrotropes, inorganic cations such as alkaline earth metals such as Ca/Mg-ions, antibacterial agents, preservatives, anti-oxidants and pH adjusters and buffering means.

Method of washing

20 Other aspects of the invention are directed to a method of washing dishware with the composition of the present invention.

The composition herein can be applied in its diluted form. Soiled dishes are contacted with an effective amount, typically from about 0.5 ml to about 20 ml (per about 25 dishes being treated), preferably from about 3ml to about 10 ml, of the detergent composition, preferably in liquid form,
25 of the present invention diluted in water. The actual amount of detergent composition used will be based on the judgment of user, and will typically depend upon factors such as the particular product formulation of the composition, including the concentration of active ingredients in the composition, the number of soiled dishes to be cleaned, the degree of soiling on the dishes, and the like. Generally, from about 0.01 ml to about 150 ml, preferably from about 3ml to about 40ml
30 of a liquid detergent composition of the invention is combined with from about 2000 ml to about 20000 ml, more typically from about 5000 ml to about 15000 ml of water in a sink having a volumetric capacity in the range of from about 1000 ml to about 20000 ml, more typically from about 5000 ml to about 15000 ml. The soiled dishes are immersed in the sink containing the diluted compositions then obtained, where contacting the soiled surface of the dish with a cloth, sponge,

or similar article cleans them. The cloth, sponge, or similar article may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface, and is typically contacted with the dish surface for a period of time ranged from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of cloth,
5 sponge, or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

Another method may comprise immersing the soiled dishes into a water bath or held under running water without any liquid dishwashing detergent. A device for absorbing liquid dishwashing detergent, such as a sponge, is placed directly into contact with a separate quantity of
10 undiluted liquid dishwashing composition for a period of time typically ranging from about 1 to about 5 seconds. The absorbing device, and consequently the undiluted liquid dishwashing composition, is then contacted individually to the surface of each of the soiled dishes to remove said soiling. The absorbing device is typically contacted with each dish surface for a period of time range from about 1 to about 10 seconds, although the actual time of application will be dependent
15 upon factors such as the degree of soiling of the dish. The contacting of the absorbing device to the dish surface is preferably accompanied by concurrent scrubbing.

Alternatively, the device may be immersed in a mixture of the hand dishwashing composition and water prior to being contacted with the dish surface, the concentrated solution is made by diluting the hand dishwashing composition with water in a small container that can
20 accommodate the cleaning device at weight ratios ranging from about 95:5 to about 5:95, preferably about 80:20 to about 20:80 and more preferably about 70:30 to about 30:70, respectively, of hand dishwashing liquid:water respectively depending upon the user habits and the cleaning task.

The dimensions and values disclosed herein are not to be understood as being strictly
25 limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

30 EXAMPLES

Test methods :

Foam test :

The foam test aims at defining the foam building potential of a detergent composition applied on a sponge. For each test product 30 g of aqueous wash solutions (2.8 dH water hardness, 20°C) of the following targeted product concentrations are prepared: 40, 30, 20, 10, 5, 1, 0.5, 0.1wt%. Synthetic dishwashing sponges (Brand : Delhaize Belgium scour sponges with grip - dimensions: length 9.5cm, width 6.5cm and height 4.5cm, item number 17152/0000) are pre-conditioned by washing them without detergent during 3 cycles of 32min at 40°C and 15dH water hardness in a laundry washing machine (Brand: Miele Softronic W3205 – Express cycle), and leaving them to dry for 2 days under a fume hood (Brand: Kötermann type 2-453-GAHB) with air flow 0.64m/sec under standard lab conditions (20-22°C, 40-60% rH).

The respective 30g wash solution is distributed equally on the soft side opposite to the scouring side of the dry sponge, allowing the wash solution to completely submerge into the sponge during 20 seconds. While wearing latex lab gloves and while holding the scouring side down, the sponge is consequently manually squeezed for 10 times with maximum power (frequency 60 squeezes per minute) after which the generated foam on the sponge is collected with a spatula in a cup allowing accurate volumetric grading. 2 replicates are run for each product concentration and collected foam volumes are averaged. For each product concentration and replicate a new dry sponge is used and all tests are run by the same expert operator. For each product the average collected foam volume for each product concentration is cumulated and indexed versus a chosen reference product in the test according to formula 1.

Formula 1 : foam index test product = (cumulative foam volume test product / cumulative foam volume reference product) * 100.

Resulting foam indexes are reported. Higher foam indexes indicate a higher foaming potential of a product when applied to a sponge.

Grease cleaning test :

A polypropylene nonwoven substrate (SMS 60g/sm – supplier: Avgol Nonwovens LTD) of dimensions 4.5cm x 4.5cm is soiled with 175-200mg of Beef Fat (composition : see table below) colored with 0.05% EGN Oil Red dye (supplier: Sigma-Aldrich). Soiled substrate is put at 21°C/35% RH for minimum 48 and max 120 hours to dry. After drying, the initial soil level is measured via weighing of the soiled substrate versus the weight of the unsoiled substrate.

Beef Fat Composition:

Ingredient	Supplier	[%, as is]
------------	----------	------------

Refined Rendered Edible Beef Tallow	Bunge North America Corporate Headquarters 11720 Borman Drive St. Louis, MO 63146	99.419
Oleic Acid, 90% (Techn)	Aldrich	0.274
Palmitic Acid, 99+%	VWR	0.207
Stearic Acid, 99+% (Gold Label)	Aldrich	0.101
	<u>Total:</u>	<u>100</u>

The grease cleaning performance is tested with a LaunderO-meter (Washtec device – supplier: Roaches International LTD). Three soiled substrates as internal replicates are put in a LaunderO-meter jar with 200g of wash solution at desired water hardness (2 dH) and product concentration (5%), together with 3 marbles for extra abrasion. Washing is done for 5 min at 35°C followed by a 5 minutes rinse with 200g of water at desired water hardness (2dH) and room temperature.

After washing and drying (minimum 48 hours at 21 °C/35% RH), the remaining soil level is measured by weighing and % grease removal is calculated as follows: ((soil weight before washing – soil weight after washing)/soil weight before washing) x 100%. The average % grease removal of the 3 internal replicates is reported as a grease cleaning index versus a chosen reference product in the test according to formula 2.

Formula 2 : grease cleaning index test product = (% grease removal test product / % grease removal reference product) * 100.

Resulting grease cleaning indexes are reported. The higher the grease cleaning index the higher the grease cleaning potential of the test product.

Test products :

% active by weight of the composition	Reference	Comparative example A	Example A
	Nil cyclic diamine, Nil C10 AO	Cyclic diamine, nil C10 AO	Cyclic diamine + C10 AO
C1213 alkyl ethoxy (0.6) sulfate (AES)	23.1%	23.1%	23.1%

C1214 dimethyl amine oxide	2.45%	2.45%	0.45%
C10 dimethyl amine oxide	-	-	2.0%
Lutensol XP80	0.46%	0.46%	0.46%
Baxxodur ECX210	-	1%	1%
NaCl	1.2%	1.2%	1.2%
Polypropyleneglycol (MW 2000)	1.6%	1.6%	1.6%
Ethanol	5.7%	5.7%	5.7%
pH (10% dilution in demi water at 20°C) – with NaOH	8	8	8
Water and minors (dye, perfume, preservative)	To 100%	To 100%	To 100%

C1213 alkyl ethoxy (0.6) sulfate (AES): C12-13 alkyl ethoxy sulfate with an average degree of ethoxylation of 0.6

Lutensol XP80: Non-ionic surfactant available from BASF

Baxxodur ECX210: mixture of 4-methylcyclohexane-1,3-diamine and 2-methylcyclohexane-1,3-diamine, available from BASF.

Test results :

The table below summarizes the grease cleaning and foaming performance of a nil cyclic diamine nil low cut amine oxide reference detergent formulation, a comparative example detergent formulation outside the scope of the invention comprising a cyclic diamine and an example detergent formulation within the scope of the invention comprising both the cyclic diamine and the low cut amine oxide. It is clear from table below that the presence of the low cut amine oxide compensates the foaming hurt induced by the cyclic diamine while not impacting on grease cleaning.

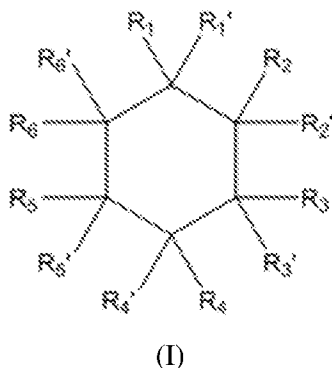
	Foam Index	Grease cleaning index
Reference	100	100
Comparative Example 1	87	129
Example 1	113	125

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean

5 “about 40 mm”.

CLAIMS

1. A hand dishwashing detergent composition comprising anionic surfactant and an amine oxide surfactant comprising a low-cut amine oxide of formula $R_aR_bR_cAO$ wherein R_a and R_b are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R_c is selected from C10 alkyls and mixtures thereof, and a cyclic diamine of Formula(I):



- wherein two of the R_s are selected from the group consisting of NH_2 , $(C1-C4)NH_2$ and mixtures thereof and the remaining R_s are independently selected from H, linear or branched alkyl or alkenyl having from 1 to 10 carbon atoms.
2. A composition according to claim 1 comprising from about 1% to about 15% by weight of the composition of the amine oxide.
 3. A composition according to any of claims 1 or 2 comprising from about 10% to about 100% by weight of the amine oxide of the low-cut amine oxide.
 4. A composition according to any of the preceding claims comprising from about 0% to about 90% by weight of the amine oxide of a mid-cut amine oxide of formula $R_dR_eR_fAO$ wherein R_d and R_e are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R_f is selected from C12-C16 alkyls and mixtures thereof.
 5. A composition according to any of the preceding claims comprising from 0.1 to 5%, preferably from 0.1 to 2% by weight of the composition of the cyclic diamine.
 6. A composition according to any of the preceding claims wherein the remaining R_s are selected from H, CH_3 and mixtures thereof.
 7. A composition according to any of the preceding claims wherein the two R_s selected from the group consisting of NH_2 , $(C1-C4)NH_2$ and mixtures thereof are in positions 1 and 3.
 8. A composition according to the any of the preceding claims wherein the cyclic diamine is selected from the group consisting of 1, 3-bis(methylamine)-cyclohexane, 2-methylcyclohexane-1,3-diamine, 4-methylcyclohexane-1,3-diamine and mixtures thereof,

preferably 2-methylcyclohexane-1,3-diamine, 4-methylcyclohexane-1,3-diamine and mixtures thereof.

9. A composition according to any of the preceding claims comprising from about 1 to about 15% by weight of the composition of the amine oxide surfactant wherein the amine oxide surfactant comprises
 - a) from about 10% to about 100% by weight of the amine oxide of the low-cut amine oxide wherein Ra and Rb are both methyl and Rc is n-decyl;
 - b) from about 0% to about 90% by weight of the amine oxide of the mid-cut amine oxide.
10. A composition according to any of the preceding claims comprising less than about 5%, more preferably less than 3% by weight of the amine oxide of an amine oxide of formula RgRhRiAO wherein Rg and Rh are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein Ri is selected from C8 alkyls and mixtures thereof.
11. A composition according to any of the preceding claims wherein the anionic surfactant comprises a sulphate anionic surfactant, preferably an alkyl sulphate and/or alkoxyated sulfate anionic surfactant, preferably an alkyl alkoxyated sulphate, preferably the alkoxyated anionic surfactant having an average alkoxylation degree of from about 0.2 to about 3, preferably from about 0.2 to about 2, most preferably from about 0.2 to about 1.0
12. A composition according to any of the preceding claims wherein the amount of anionic surfactant is from about 10% to 40% by weight of the composition.
13. A composition according to any of the preceding claims wherein the weight ratio of the anionic surfactant to the amine oxide surfactant is from about 1:1 to about 10:1.
14. A composition according to any of the preceding claims wherein the composition comprises less than 2% by weight of the composition of non ionic surfactant.
15. A process for making a hand dishwashing detergent composition comprising a low-cut and mid-cut amine oxide according to any of claims 4 to 14 comprising the step of delivering the low-cut and mid-cut amine oxide from different feed stocks.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/037816

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D1/83 C11D3/30
ADD. C11D1/75

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	WO 2006/020010 A1 (PROCTER & GAMBLE [US]; HECHT STACIE ELLEN [US]; SHI JICHUN [US]; NEIHO) 23 February 2006 (2006-02-23) claims examples C,D page 12, line 1 - line 14 page 1, line 32 - line 36 page 3, line 8 - line 10 page 4, line 25 - page 5, line 17 -----	1-15
A	EP 2 940 115 A1 (PROCTER & GAMBLE [US]) 4 November 2015 (2015-11-04) claims examples page 3, line 12 - page 4, line 18 page 5, line 53 - page 6, line 16 ----- -/--	1-15



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

15 August 2017

Date of mailing of the international search report

23/08/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Neys, Patricia

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/037816

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00/46330 A1 (PROCTER & GAMBLE [US]; OFUSU ASANTE KOFI [US]; CLARKE JOANNA MARGARET) 10 August 2000 (2000-08-10) claims examples page 18, line 9 - page 11, line 21 page 5, line 17 - line 30 page 7, line 1 - line 9 page 1, line 10 - page 15 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/037816

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006020010	A1	23-02-2006	CA 2573692 A1 23-02-2006
		CN 1989232 A 27-06-2007	
		EP 1771536 A1 11-04-2007	
		JP 2008507611 A 13-03-2008	
		US 2006019851 A1 26-01-2006	
		WO 2006020010 A1 23-02-2006	

EP 2940115	A1	04-11-2015	AR 100233 A1 21-09-2016
		CA 2956670 A1 05-11-2015	
		EP 2940115 A1 04-11-2015	
		JP 2017513986 A 01-06-2017	
		US 2015315522 A1 05-11-2015	
		WO 2015167836 A1 05-11-2015	

WO 0046330	A1	10-08-2000	AR 017745 A1 12-09-2001
		AU 2874500 A 25-08-2000	
		EP 1151069 A1 07-11-2001	
		JP 2002536496 A 29-10-2002	
		US 6521577 B1 18-02-2003	
		WO 0046330 A1 10-08-2000	
