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(54) Title: METHOD OF MANUAL DISHWASHING

(57) Abstract: A method of manually washing dishware in soft water comprising the step of delivering a cleaning composition to a volume of soft water to form a wash liquor and immersing the dishware in the liquor wherein the detergent composition comprises anionic surfactant, amine oxide surfactant and an amphiphilic alkoxyated polyalkyleneimine.



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METHOD OF MANUAL DISHWASHING

FIELD OF THE INVENTION

The present invention relates to a method of manually washing dishware using a detergent
5 composition comprising anionic surfactant, amine oxide surfactant including a low-cut amine
oxide and an amphiphilic alkoxyated polyalkyleneimine. The method provides very good
cleaning with long lasting suds in soft water.

BACKGROUND OF THE INVENTION

10 The performance of hand dishwashing cleaning compositions can be linked to the hardness of
the water used for the dishwashing process. Different compositions perform different under
different water hardness.

Traditionally manual dishwashing has been performed by filling a sink with water, adding a
15 dishwashing detergent to create a soapy solution, immersing the soiled articles in the solution,
scrubbing the articles and rinsing to remove the remaining soils and remove the suds generated
from the soapy solution from the washed articles. Users associate the presence of suds in a
washing solution with good cleaning.

20 There is a need to provide a method of manual dishwashing that provides good cleaning and at
the same time long-lasting suds when the manual dishwashing is performed with soft water.

SUMMARY OF THE INVENTION

According to a first aspect of the invention, there is provided a method of manually washing
25 dishware with soft water using a specific cleaning composition.

The composition comprises anionic surfactant, amine oxide surfactant, including low and mid
cut amine oxide surfactants and an amphiphilic alkoxyated polyalkyleneimine. The
composition used in the method of the invention provides good cleaning and long lasting suds.

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The composition used in the method of the invention is sometimes herein referred to as “the
composition of the invention”.

By "soft water" is herein meant water having a hardness equal or less than 10 gpg, preferably less than 5 gpg (grains per gallon, i.e. a unit of water hardness defined as 1 grain (64.8 milligrams) of calcium carbonate dissolved in 1 US gallon of water (3.785412 L)).

- 5 The composition preferably comprises from about 3 to about 15%, preferably from about 5 to about 12% by weight of the composition of amine oxide surfactant. The amine oxide surfactant is a mixture of amine oxides comprising a low-cut amine oxide and a mid-cut amine oxide.

The amine oxide of the composition of the invention comprises:

- 10 a) from about 5% to about 40%, preferably from 10% to about 30% by weight of the amine oxide of low-cut amine oxide of formula R1R2R3AO wherein R1 and R2 are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R3 is selected from C10 alkyls and mixtures thereof; and
- b) from 60% to 95%, preferably from 70% to about 90% by weight of the amine oxide
15 of mid-cut amine oxide of formula R4R5R6AO wherein R4 and R5 are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R6 is selected from C12-C16 alkyls and mixtures thereof.

The amphiphilic alkoxyated polyalkyleneimine is an alkoxyated polyethyleneimine polymer
20 comprising a polyethyleneimine backbone. The polyethyleneimine backbone has a molecular weight of from about 400 to about 5,000, preferably from about 500 to about 2,000 weight average molecular weight. The alkoxyated polyethyleneimine polymer further comprises:

- (1) one or two alkoxylation modifications per nitrogen atom by a polyalkoxylyene chain
25 having an average of about 1 to about 50, preferably about 10 to about 45 alkoxy moieties per modification, wherein the terminal alkoxy moiety of the alkoxylation modification is capped with hydrogen, a C₁-C₄ alkyl or mixtures thereof, preferably the alkoxylation modification is capped with hydrogen; or
- (2) an addition of one C₁-C₄ alkyl moiety and one or two alkoxylation modifications per
30 nitrogen atom by a polyalkoxylyene chain having an average of about 1 to about 50, preferably about 10 to about 45 alkoxy moieties per modification wherein the terminal alkoxy moiety is capped with hydrogen, a C₁-C₄ alkyl or mixtures thereof, preferably the alkoxylation modification is capped with hydrogen; or
- (3) a combination thereof; and

wherein the alkoxy moieties comprises ethoxy (EO) and/or propoxy (PO) and/or butoxy and wherein when the alkoxylation modification comprises EO it also comprises PO or BO.

Preferably, the weight average molecular weight per polyalkoxylene chain is from 400 to 8,000 preferably from 600 to 4,000, more preferably 800 to 2,000. Preferably, the weight average molecular weight of the alkoxyated polyethyleneimine is from 8,000 to 40,000, preferably 10,000 to 30,000.

If the polyalkoxylene chain comprises an ethoxy and a propoxy moiety, the propoxy moiety is preferably in a terminal position. If the polyalkoxylene chain comprises an ethoxy and a butoxy moiety but no propoxy moiety, the butoxy moiety is preferably in a terminal position.

Preferably, the polyalkoxylene chain comprises ethoxy and propoxy moieties, more preferably in
5 a number ratio of 1:1 to 2:1.

Preferred for use herein are alkoxyated polyalkyleneimine in which the number of ethoxy moieties of a polyalkoxylene chain is from 22 to 26, the number of propoxy moieties is from 14 to 18 and preferably the polyalkoxylene chain is free of butoxy moieties. Preferably this
10 alkoxyated polyalkyleneimine polymer has a molecular weight of from 25,000 to about 30,000. More preferred for use herein are alkoxyated polyalkyleneimine in which the number of ethoxy moieties of a polyalkoxylene chain is from 8 to 12, and the number of propoxy moieties is from 5 to 9 and preferably the polyalkoxylene chain free of butoxy moieties. Preferably this
15 alkoxyated polyalkyleneimine polymer has a molecular weight of from 10,000 to about 15,000. Preferably these preferred alkoxyated polymers have a polyethyleneimine backbone with a molecular weight of from about 400 to about 800.

In a preferred low-cut amine oxide for use herein R3 is n-decyl. In another preferred low-cut amine oxide for use herein R1 and R2 are both methyl. In an especially preferred low-cut amine
20 oxide for use herein R1 and R2 are both methyl and R3 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 R7R8R9AO wherein R7 and R8 are

selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R9 is selected from C8 alkyls and mixtures thereof. Compositions comprising higher levels of R7R8R9AO tend to be instable.

5 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 alkyl 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,
10 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
15 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 composition of the invention comprises from 0.1% to about 2%, more preferably
20 less than 1.5% 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 the use of a
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i) low-cut amine oxide of formula R1R2R3AO wherein R1 and R2 are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R3 is selected from C10 alkyls and mixtures thereof; and
ii) an amphiphilic alkoxyated polyalkyleneimine
30 in manual dishwashing to provide suds longevity in soft water. Preferably, the hand dishwashing composition comprises anionic surfactant and amine oxide surfactant in a ratio of from about 5:1 to about 1:1, preferably 4:1 to 2:1, most preferably 3.5:1 to 2.5:1.

The elements of the method and composition of the invention described in connection with the first aspect of the invention apply *mutatis mutandis* to the second aspect of the invention.

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

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DETAILED DESCRIPTION OF THE INVENTION

The present invention envisages a method of manually washing dishware with soft water using a cleaning composition, preferably in liquid form. The detergent composition comprises a surfactant system comprising anionic and amine oxide surfactant and an amphiphilic alkoxyated polyalkyleneimine. It provides very good cleaning and long lasting suds in soft water.

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Method of the invention

The method of the invention comprises the steps of:

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i) delivering a cleaning composition to a volume of soft water (i.e., water having a hardness of less than 10 gpg, preferably less than 5 gpg) to form a wash liquor. The concentration of the cleaning composition is preferably from about 0.05% to about 1%, more preferably from 0.08 to 2% by weight of the wash liquor.

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ii) immersing the dishware into the wash liquor and cleaning the dishware, preferably with a cleaning implement; and

iii) optionally but preferably rinsing the dishware.

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The washing temperature can be any temperature preferably selected from about 10°C to about 60°C, more preferably from about 20°C to about 55°C, most preferably from about 30°C to about 50° C.

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In the method of the invention the composition is applied in diluted form. Soiled dishware is 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 cleaning composition, preferably in liquid form, of the present invention diluted in water. The actual amount of cleaning 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 dishware 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 of a liquid 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 water used is soft water having a hardness of less than 10 gpg, preferably less than 5 gpg. The soiled dishware is immersed in the sink containing the diluted compositions then obtained, where contacting the soiled surface of the dishware with a cloth, sponge, or similar article cleans them. The cloth, sponge, or similar article may be immersed in the washing liquor prior to being contacted with the dishware surface, and is typically contacted with the dishware 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, sponge, or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dishware surface. The dishware can be optionally rinsed.

15 The cleaning composition

The cleaning composition is a hand dishwashing cleaning composition, 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 between 3 and 14, more preferably between 4 and 13, more preferably between 6 and 12 and most preferably between 8 and 10. 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 comprise 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.

Viscosity

The composition of the present invention can be Newtonian or non-Newtonian liquid, preferably Newtonian, with a viscosity of between 10 centipoises (cps) and 5,000cps at 20 °C and, alternatively between 50cps and 2,000cps, or between 100cps and 1,500cps, or between 150cps and 1,000cps, alternatively combinations thereof.

Viscosity is measured with a BROOFIELD DV-E viscometer, at 20°C, spindle number 31. The following rotations per minute (rpm) should be used depending upon the viscosity: Between 300 cps to below 500 cps is at 50 rpm; between 500 cps to less than 1,000 cps is at 20 rpm; from 1,000 cps to less than 1,500 cps at 12 rpm; from 1,500 cps to less than 2,500 cps at 10 rpm; from 2,500 cps, and greater, at 5 rpm. Those viscosities below 300 cps are measured at 12 rpm with spindle number 18.

Amine oxide surfactant

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The amine oxide surfactant in combination with the amphiphilic alkoxyated polyalkyleneimine improves the cleaning and the longevity of suds under soft water conditions.

Low-cut amine oxide

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Within the meaning of the present invention “low-cut amine oxide” means an amine oxide of formula: R1R2R3AO wherein R1 and R2 are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R3 is selected from C10 alkyls and mixtures thereof.

25 Mid-cut amine oxide

Within the meaning of the present invention “mid-cut amine oxide” means an amine oxide of formula: R4R5R6AO wherein R4 and R5 are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R6 is selected from C12-C16 alkyls and mixtures thereof.

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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.

- 5 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.
- 10 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.
- 15 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
- 20 average 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 = $(x_1 * \text{alkoxylation degree of surfactant 1} + x_2 * \text{alkoxylation degree of surfactant 2} + \dots) / (x_1 + x_2 + \dots)$

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 composition of the present invention is a
- 30 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 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.

- 5 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.
- 10 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 (%) = $[(x_1 * \text{wt\% branched alcohol 1 in alcohol 1} + x_2 * \text{wt\% branched alcohol 2 in alcohol 2} + \dots) / (x_1 + x_2 + \dots)] * 100$

15

wherein x_1 , x_2 , 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.

20

- 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, more preferably from 0.2 to 1 and preferably an average level of branching of from about 5% to about 40%.
- 25

- 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, preferably 0.2 to 1 and preferably a level of branching of from about 5% to about 40%.
- 30

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 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.

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 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), 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.

5 Nonionic surfactant, when present, is comprised in an amount of less than 2%, preferably less than 1.5% 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 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
 10 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 2 to 18 moles, preferably 2 to 15, more preferably 5-12 of ethylene oxide per mole of alcohol.

15

Zwitterionic surfactant

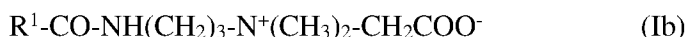
Other suitable surfactants include betaines, such as alkyl betaines, alkylamidobetaine, amidazoliniumbetaine, sulfobetaine (INCI Sultaines) as well as the Phosphobetaine and
 20 preferably meets formula I:

$R^1-[CO-X(CH_2)_n]_x-N^+(R^2)(R^3)-(CH_2)_m-[CH(OH)-CH_2]_y-Y$ (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;
 25 X is NH, NR⁴ with C1-4 Alkyl residue R⁴, O or S,
 n a number from 1 to 10, preferably 2 to 5, in particular 3,
 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.
 30 m a number from 1 to 4, in particular 1, 2 or 3,
 y 0 or 1 and
 Y is COO, SO₃, OPO(OR⁵)O or P(O)(OR⁵)O, whereby R⁵ 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);

5



10 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
 15 INCI]: Almondamidopropyl of betaines, Apricotamidopropyl betaines, Avocamidopropyl of betaines, Babassamidopropyl 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
 20 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
 25 betaines, Myristyl of betaines, Oleamidopropyl betaines, Oleamidopropyl Hydroxysultaine, Oleyl of betaines, Olivamidopropyl of betaines, Palmamidopropyl betaines, Palm itamidopropyl betaines, Palmitoyl Carnitine, Palm Kernelamidopropyl betaines, Polytetrafluoroethylene Acetoxypentyl of betaines, Ricinoleamidopropyl betaines, Sesamidopropyl betaines, Soyamidopropyl betaines, Stearamidopropyl betaines, Stearyl of betaines,
 30 Tallowamidopropyl betaines, Tallowamidopropyl Hydroxysultaine, Tallow of betaines, Tallow Dihydroxyethyl of betaines, Undecylenamidopropyl betaines and Wheat Germamidopropyl betaines.

A preferred betaine is, for example, Cocoamidopropylbetain.

Amphiphilic alkoxyated polyalkyleneimine polymer

5 Amphiphilic alkoxyated polyalkyleneimine

The composition of the invention comprises from about 0.1% to about 2%, preferably from more than about 0.5% to about 1.5% by weight of the composition of an amphiphilic alkoxyated polyalkyleneimine, preferably an amphiphilic alkoxyated polyethyleneimine polymer.

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Amphiphilic alkoxyated polyethyleneimine polymers will comprise ethoxy (EO) and/or propoxy (PO) and/or butoxy (BO) groups within their alkoxylation chains, when comprising EO also comprising PO and/or BO. Preferred amphiphilic alkoxyated polyethylene polymers comprise EO and PO groups within their alkoxylation chains. Hydrophilic alkoxyated polyethyleneimine polymers solely comprising ethoxy (EO) units within the alkoxylation chain are outside the scope of this invention.

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The amphiphilic alkoxyated polyethyleneimine polymer of the composition of the invention has a polyethyleneimine backbone having from about 400 to about 5,000 weight average molecular weight, preferably from about 400 to about 2,000 weight average molecular weight, even more preferably from about 400 to about 1,000 weight average molecular weight, most preferably about 600 weight average molecular weight.

20

The alkoxylation chains within the amphiphilic alkoxyated polyethyleneimine polymer of the present composition have from about 400 to about 3,000 weight average molecular weight, preferably from about 600 to about 2,500 weight average molecular weight, more preferably from about 750 to about 1,000 weight average molecular weight, most preferably about 850 weight average molecular weight per alkoxyated chain.

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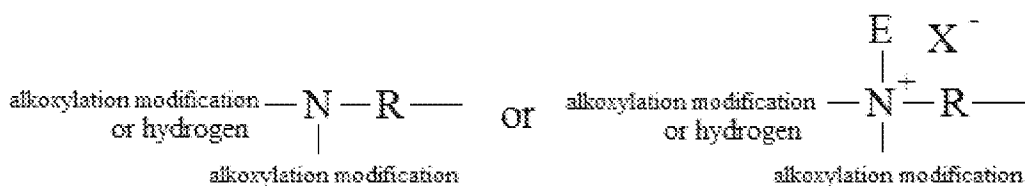
The amphiphilic alkoxyated polyethyleneimine polymer of the present composition have from about 8,000 to about 40,000 weight average molecular weight, preferably from about 9,000 to about 30,000 weight average molecular weight, more preferably from about 10,000 to about 15,000 weight average molecular weight.

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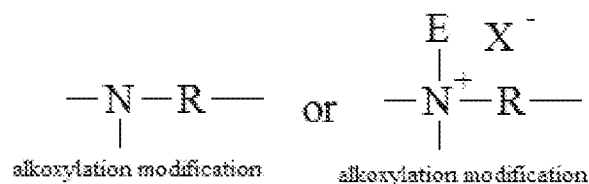
Another preferred amphiphilic alkoxyated polyethyleneimine polymer for use herein has a weight average molecular weight per polyalkoxylene chain of from 400 to 8,000 preferably from 600 to 4,000, more preferably 800 to 2,000. Preferably, the weight average molecular weight of the alkoxyated polyethyleneimine is from 8,000 to 40,000, preferably 10,000 to 30,000, especially preferred is an amphiphilic alkoxyated polyethyleneimine polymer with a weight average molecular weight of the alkoxyated polyethyleneimine is from 25,000 to 30,000 and a weight average molecular weight per polyalkoxylene chain of from 1,500 to 2,500.

The alkoxylation of the polyethyleneimine backbone includes: (1) one or two alkoxylation modifications per nitrogen atom, dependent on whether the modification occurs at a internal nitrogen atom or at an terminal nitrogen atom, in the polyethyleneimine backbone, the alkoxylation modification consisting of the replacement of a hydrogen atom by a polyalkoxylene chain having an average of about 1 to about 50 alkoxy moieties per modification, wherein the terminal alkoxy moiety of the alkoxylation modification is capped with hydrogen, a C₁-C₄ alkyl or mixtures thereof; or (2) an addition of one C₁-C₄ alkyl moiety and one or two alkoxylation modifications per nitrogen atom, dependent on whether the substitution occurs at a internal nitrogen atom or at an terminal nitrogen atom, in the polyethyleneimine backbone, the alkoxylation modification consisting of the replacement of a hydrogen atom by a polyalkoxylene chain having an average of about 1 to about 50 alkoxy moieties per modification wherein the terminal alkoxy moiety is capped with hydrogen, a C₁-C₄ alkyl or mixtures thereof, preferably hydrogen; or (3) a combination thereof.

For example, but not limited to, below is shown possible modifications to terminal nitrogen atoms in the polyethyleneimine backbone where R represents an ethylene spacer and E represents a C₁-C₄ alkyl moiety and X⁻ represents a suitable water soluble counterion.



Also, for example, but not limited to, below is shown possible modifications to internal nitrogen atoms in the polyethyleneimine backbone where R represents an ethylene spacer and E represents a C₁-C₄ alkyl moiety and X⁻ represents a suitable water soluble counterion.



The alkoxylation modification of the polyethyleneimine backbone consists of the replacement of a hydrogen atom by a polyalkoxylene chain having an average of about 1 to about 50 alkoxy moieties, preferably from about 5 to about 45 alkoxy moieties, most preferably from about 10 to about 20 alkoxy moieties. The alkoxy moieties are selected from ethoxy (EO), propoxy (PO), butoxy (BO), and mixtures thereof. Alkoxy moieties solely comprising ethoxy units are outside the scope of the invention though. Preferably, the polyalkoxylene chain is selected from ethoxy/propoxy block moieties. More preferably, the polyalkoxylene chain is ethoxy/propoxy block moieties having an average degree of ethoxylation from about 3 to about 30 and an average degree of propoxylation from about 1 to about 20, more preferably ethoxy/propoxy block moieties having an average degree of ethoxylation from about 5 to about 15 and an average degree of propoxylation from about 5 to about 10, or alternatively an average degree of ethoxylation from about 20 to about 30 and an average degree of propoxylation from about 10 to about 20.

More preferably the ethoxy/propoxy block moieties have a relative ethoxy to propoxy unit ratio between 3 to 1 and 1 to 1, preferably between 2 to 1 and 1 to 1. Most preferably the polyalkoxylene chain is the ethoxy/propoxy block moieties wherein the propoxy moiety block is the terminal alkoxy moiety block.

The modification may result in permanent quaternization of the polyethyleneimine backbone nitrogen atoms. The degree of permanent quaternization may be from 0% to about 30% of the polyethyleneimine backbone nitrogen atoms. It is preferred to have less than 30% of the polyethyleneimine backbone nitrogen atoms permanently quaternized. Most preferably the degree of quaternization is 0%.

A preferred polyethyleneimine has the general structure of formula (I):

Alternatively the polyethyleneimine has the general structure of formula (I) wherein the polyethyleneimine backbone has a weight average molecular weight of about 600, n of formula (I) has an average of about 24, m of formula (I) has an average of about 16 and R of formula (I) is hydrogen. The degree of permanent quaternization of formula (I) is 0% of the polyethyleneimine backbone nitrogen atoms. The molecular weight of this polyethyleneimine preferably is about from about 27,500 to 28,500.

These polyethyleneimines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, and the like, as described in more detail in WO 2007/135645.

Organic Solvents

The present compositions may optionally comprise an organic solvent. Suitable organic solvents include C₄₋₁₄ ethers and diethers, polyols, glycols, alkoxyated glycols, C₆₋₁₆ glycol ethers, alkoxyated aromatic alcohols, aromatic alcohols, aliphatic linear or branched alcohols, alkoxyated aliphatic linear or branched alcohols, alkoxyated C₁₋₅ alcohols, C₈₋₁₄ alkyl and cycloalkyl hydrocarbons and halohydrocarbons, and mixtures thereof. Preferably the organic solvents include alcohols, glycols, and glycol ethers, alternatively alcohols and glycols. In one embodiment, the liquid detergent composition comprises from 0% to less than 50% of a solvent by weight of the composition. When present, the liquid detergent composition will contain from 0.01% to 20%, alternatively from 0.5% to 15%, alternatively from 1% to 10% by weight of the liquid detergent composition of said organic solvent. Non-limiting examples of specific solvents include propylene glycol, polypropylene glycol, propylene glycol phenyl ether, ethanol, and combinations thereof. In one embodiment, the composition comprises from 0.01% to 20% of an organic solvent by weight of the composition, wherein the organic solvent is selected from glycols, polyalkyleneglycols, glycol ethers, ethanol, and mixtures thereof.

Hydrotrope

The composition herein optionally comprises a hydrotrope in an effective amount, i.e. from 0 % to 15%, or from 0.5 % to 10 % , or from 1 % to 6 % , or from 0.1% to 3%, or combinations

thereof, so that the liquid dish detergent compositions are compatible or more compatible in water. Suitable hydrotropes for use herein include anionic-type hydrotropes, particularly sodium, potassium, and ammonium xylene sulfonate, sodium, potassium and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof, as disclosed in U.S. Patent 3,915,903. In one embodiment, the composition of the present invention is isotropic. An isotropic composition is distinguished from oil-in-water emulsions and lamellar phase compositions. Polarized light microscopy can assess whether the composition is isotropic. See e.g., *The Aqueous Phase Behaviour of Surfactants*, Robert Laughlin, Academic Press, 1994, pp. 538-542. In one embodiment, an isotropic dish detergent composition is provided. In one embodiment, the composition comprises 0.1% to 3% of a hydrotrope by weight of the composition, preferably wherein the hydrotrope is selected from sodium, potassium, and ammonium xylene sulfonate, sodium, potassium and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof.

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

EXAMPLES

25 Evaluation of the suds mileage performance in hand dish detergent compositions

The suds mileage performance of hand dishwashing detergent compositions (Examples A-F) was assessed under dilute conditions (detergent concentration: 0.12 wt%) according to the protocol described herein. Suds mileage performance of the different compositions comprising n-C10 dimethyl amine oxide (B), alkoxyated polyethyleneimine (C, D), or mixtures thereof (E,F) has been assessed versus a nil n-C10 dimethyl amine oxide nil alkoxyated polyethyleneimine reference composition A at 35 °C and 46 °C in soft water hardness condition (2 gpg) in presence of a greasy soil and averaged. Compositions E and F comprising a mixture of both n-C10

dimethyl amine oxide and alkoxyated polyethyleneimine according to the invention clearly show an improved suds mileage performance compared to comparative examples A – D outside the scope of invention, solely comprising one or none of the n-C10 dimethyl amine oxide or alkoxyated polyethyleneimine compounds.

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Level (wt% - as 100% active)	A	B	C	D	E	F
NaAE0.6S	22.5%	22.5%	22.5%	22.5%	22.5%	22.5%
n-C12-14 Di Methyl Amine Oxide	6.1%	5.1%	6.1%	6.1%	5.1%	5.1%
n-C10 Di Methyl Amine Oxide (DMAO)	-	1%	-	-	1%	1%
Neodol 91-8	1%	1%	1%	1%	1%	1%
Lutensol XP80	0.4%	0.4%	0.4%	0.4%	0.4%	0.4%
Alkoxyated Polyethyleneimine 1 (PEI600EO10PO7)	-	-	1%	-	1%	-
Alkoxyated Polyethyleneimine 2 (PEI600EO24PO16)	-	-	-	1%	-	1%
Sodium Chloride	0.7%	0.7%	0.7%	0.7%	0.7%	0.7%
Na3-citrate.2H2O	1%	1%	1%	1%	1%	1%
Poly Propylene Glycol	0.9%	1%	0.7%	1.1%	0.7%	1.2%
Ethanol	2.2%	2.2%	1.7%	1.7%	1.6%	1.6%
Sodium Hydroxide	0.26%	0.27%	0.25%	0.26%	0.25%	0.26%
Minors + water	To 100 %	To 100 %	To 100 %	To 100 %	To 100%	To 100%
pH (@ 10% solution)	9	9	9	9	9	9

PEI600EO10PO7 : Polyethyleneimine backbone with MW about 600, comprising EO – terminal PO block polyalkoxylate side chains comprising each on average 10 EO and 7 PO units and hydrogen capped, MW 12417.

PEI600EO24PO16 : Polyethyleneimine backbone with MW about 600, comprising EO – terminal PO block polyalkoxylate side chains comprising each on average 24 EO and 16 PO units and hydrogen capped, MW 28000.

	Suds mileage performance 35°C	Suds mileage performance 46°C	Avg Suds mileage performance
Reference : Composition A (nil n-C10 DMAO – nil PEI)	100	100	100
Composition B (n-C10 DMAO)	95	96	95
Composition C (nil n-C10 DMAO – PEI600EO10PO7)	103	102	102
Composition D (nil n-C10 DMAO – PEI600EO24PO16)	107	104	105
Composition E (n-C10 DMAO – PEI600EO10PO7)	108	109	109
Composition F (n-C10 DMAO – PEI600EO24PO16)	107	111	109

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Suds mileage Testing protocol:

The evolution of the foam volume generated by a certain solution of dishwashing liquid is followed at specified soft water hardness (2 gpg), solution temperature and cleaning composition concentration, under influence of periodic soil injections. Data are compared and expressed versus a reference product as a suds mileage index (reference product has suds mileage index of 100).

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A defined amount of dishwashing product depending on the targeted product concentration is dispensed through a pipette with a flow rate of 0.67 ml / sec at a height of 37 cm above the sink bottom surface into a water stream that starts filling up a sink (dimensions: cylinder - Diameter 300 mm & height 288 mm) to 4L with a constant pressure of 4 bar. With this pressure an initial suds volume is generated in the sink.

After recording the initial foam volume (average foam height * sink surface area) a fixed amount of soil (6 ml) will be injected almost instantaneously in the middle of the sink, while a paddle (metal blade 10 x 5 cm, positioned in the middle of the sink at the air liquid interface under an angle of 45 degrees) will rotate 20 times into the solution at 85 rpm. This step is followed immediately by another measurement of the total suds volume. The soil injecting, paddling and measuring steps are repeated until the measured foam volume reaches a minimum level, which is set at 400cm³. The amount of soil additions needed to get to that level is considered as the mileage (suds longevity) of that specific sample.

The complete process is repeated 20 times per sample and per testing condition (temperature). As a final result the average mileage of the 20 replicates is calculated for each sample and averaged across testing conditions. Comparing the average mileage of the test sample versus that of the reference sample, indicates the performance of the test sample versus that reference sample, and is expressed as a suds mileage index, calculated as (average number of soil additions of test sample / average number of soil additions of reference sample)*100.

Soil composition :

Ingredient	Weight %
Crisco oil	12.730
Crisco shortening	27.752
Lard	7.638
Refined Rendered Edible Beef Tallow	51.684
Oleic Acid, 90% (Techn)	0.139
Palmitic Acid, 99+%	0.036
Stearic Acid, 99+%	0.021

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 “about 40 mm”.

CLAIMS

What is claimed is:

1. A method of manually washing dishware in soft water comprising the step of delivering a cleaning composition to a volume of soft water to form a wash liquor and immersing the dishware in the liquor wherein the detergent composition comprises anionic surfactant and amine oxide surfactant and wherein the amine oxide surfactant comprises:
 - a) from about 5% to about 40% by weight of the amine oxide of low-cut amine oxide of formula R₁R₂R₃AO wherein R₁ and R₂ are selected from hydrogen, C₁-C₄ alkyls and mixtures thereof and wherein R₃ is selected from C₁₀ alkyls and mixtures thereof; and
 - b) from 60% to 95% by weight of the amine oxide of mid-cut amine oxide of formula R₄R₅R₆AO wherein R₄ and R₅ are selected from hydrogen, C₁-C₄ alkyls and mixtures thereof and wherein R₆ is selected from C₁₂-C₁₆ alkyls and mixtures thereofand an amphiphilic alkoxyated polyalkyleneimine wherein the amphiphilic alkoxyated polyalkyleneimine is an alkoxyated polyethyleneimine polymer comprising a polyethyleneimine backbone having from about 400 to about 5,000 weight average molecular weight and the alkoxyated polyethyleneimine polymer further comprises:
 - (1) one or two alkoxylation modifications per nitrogen atom by a polyalkoxylene chain having an average of about 1 to about 50 alkoxy moieties per modification, wherein the terminal alkoxy moiety of the alkoxylation modification is capped with hydrogen, a C₁-C₄ alkyl or mixtures thereof;
 - (2) an addition of one C₁-C₄ alkyl moiety and one or two alkoxylation modifications per nitrogen atom by a polyalkoxylene chain having an average of about 1 to about 50 alkoxy moieties per modification wherein the terminal alkoxy moiety is capped with hydrogen, a C₁-C₄ alkyl or mixtures thereof; or
 - (3) a combination thereof; andwherein the alkoxy moieties comprises ethoxy (EO) and/or propoxy (PO) and/or butoxy (BO) and wherein when the alkoxylation modification comprises EO it also comprises PO or BO.
2. A method according to claim 1 wherein the weight average molecular weight per polyalkoxylene chain is from 400 to 8,000.

3. A method according to claim 1 or 2 wherein the weight average molecular weight of the alkoxyated polyethyleneimine is from 8,000 to 40,000.
4. A method according to any of the preceding claims wherein the polyalkoxylene chain comprises a propoxy moiety in a terminal position.
5. A method according to any of the preceding claims wherein the polyalkoxylene chain comprises ethoxy and propoxy moieties in a ratio of 1:1 to 2:1.
6. A method according to any of the preceding claims wherein the number of ethoxy moieties of a polyalkoxylene chain is from 22 to 26, and the number of propoxy moieties is from 14 to 18 and preferably the polyalkoxylene chain is free of butoxy moieties.
7. A method according to any of the preceding claims wherein the number of ethoxy moieties of a polyalkoxylene chain is from 8 to 12, and the number of propoxy moieties is from 5 to 9 and preferably the polyalkoxylene chain free of butoxy moieties.
8. A method according to any of the preceding claims wherein R3 is n-decyl and R1 and R2 are both methyl.
9. A method according to any of the preceding claims comprising from about 3 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 30% by weight of the amine oxide of the low-cut amine oxide wherein R1 and R2 are both methyl and R3 is n-decyl;
 - b) from about 70% to about 90% by weight of the amine oxide of the mid-cut amine oxide.
10. A method 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 R7R8R9AO wherein R7 and R8 are selected from hydrogen, C1-C4 alkyls and mixtures thereof and wherein R9 is selected from C8 alkyls and mixtures thereof.
11. A method according to any of the preceding claims wherein the anionic surfactant and the amine oxide surfactant are in a weight ratio of from about 5:1 to about 1:1, preferably from about 4:1 to about 2:1.

12. A method according to any of the preceding claims wherein the composition comprises from 0.1 to 2% by weight of the composition of the alkoxyated polyalkyleneimine.
13. A method according to any of the preceding claims further comprising a poly alkylene glycol having a molecular weight greater than 1,000, preferably poly propylene glycol.
14. A method according to any of the preceding claims wherein the composition comprises a salt, preferably sodium chloride.
15. A method according to any of the preceding claims wherein the composition comprises an alcohol, preferably ethanol.
16. A method according to any of the preceding claims wherein the composition comprises a hydrotrope, preferably sodium cumene sulfonate.
- 5 17. A method 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 an alkyl 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.
18. A method according to any of the preceding claims wherein the amount of anionic surfactant is from about 10% to 40% by weight of the composition.
19. A method according to any of the preceding claims wherein the composition comprises from 0.1% to 2% by weight of the composition of non ionic surfactant.
20. A method according to any of the preceding claims wherein the total level of surfactant is from about 10 to 40%, preferably from 20 to 35% by weight of the composition.
21. A method according to any of the preceding claims wherein the composition has a pH measured at 10% dilution in distilled water at 20°C of from about 8 to about 10.
- 10 22. Use of the composition of the method of any of the preceding claims to prolong the duration of suds in soft water in manual dishwashing.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/027853

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D1/83 C11D3/37
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	US 2009/124531 A1 (DANZIGER JAMES LEE [US] ET AL) 14 May 2009 (2009-05-14) example 10 -----	1-22
A	US 2008/300158 A1 (SCHUTZ TRISTAN [BE] ET AL) 4 December 2008 (2008-12-04) claims 1-18; table A -----	1-22
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 26 June 2017	Date of mailing of the international search report 03/07/2017
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Richards, Michael
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/027853

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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International application No

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