

(19)



(11)

EP 2 963 100 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

06.01.2016 Bulletin 2016/01

(51) Int Cl.:

C11D 1/825 ^(2006.01)

C11D 1/72 ^(2006.01)

C11D 1/722 ^(2006.01)

(21) Application number: **14175880.5**

(22) Date of filing: **04.07.2014**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

• **Holtin, Karsten**

8908 Hedingen (CH)

• **Tachikawa, Kaoru**

8902 Urdorf (CH)

(71) Applicant: **Kolb Distribution Ltd.**

8908 Hedingen (CH)

(74) Representative: **Fabry, Bernd**

IP2 Patentanwalts GmbH

Schlossstrasse 523

41238 Mönchengladbach (DE)

(72) Inventors:

• **Kolano, Christoph**

8907 Wettswil (CH)

(54) **Liquid rinse aid compositions**

(57) Suggested is a liquid rinse aid composition, comprising a blend of two non-ionic surfactants having simultaneously good rinsing, drying, streak-free, anti-filming and anti-spotting performance on substrates and also showing compared to the state of the art a superior water run-off behaviour.

EP 2 963 100 A1

Description**FIELD OF INVENTION**

5 **[0001]** The present invention belongs to the area of detergents and refers to a new blend of surfactants, rinse aid compositions comprising them and their use as rinse aid surfactants.

STATE OF THE ART

10 **[0002]** Nowadays, higher demands are placed on machine-washed dishes than on manually washed dishes. For example, even dishes completely cleaned of food residues are not assessed as perfect if, after machine dishwashing, they still have whitish spots based on water hardness or other mineral salts which, due to a lack of wetting agent, originate from dried water drops. In order to obtain brilliantly clear and spot-free dishes, rinse aids are therefore used. The addition of liquid or solid rinse aid ensures that the water runs off from the ware as completely as possible, meaning that the wide variety of surfaces are residue-free and shiny at the end of the wash programme. Standard commercial rinse aids are mixtures of non-ionic surfactants, solubility promoters, organic acids solvents, polymers and dyes, water and optionally preservatives and fragrances. The aim of the surfactants in these compositions consists in influencing the interfacial tension of the water in such a way that it can run off from the ware in the thinnest possible, coherent film so that no water drops, streaks or films are left behind during the subsequent drying process (so-called wetting effect). A distinction is generally made here between two types of deposits: firstly, the so-called "spotting" is investigated, which arises as a result of drying water drops, and secondly "filming" is evaluated, i.e. layers which are formed by the drying of thin water films containing food rests or increased salt concentration in rest water. For the evaluation, test persons are currently used who visually evaluate the parameters of "spotting" and "filming" on cleaned objects, e.g. plates, glasses, knives etc. Modern dishwashing detergents therefore comprise rinse aids in order to improve the run-off of water from the surfaces of the ware. However, there are rinse aids which do not dry equally as well on all substrates, such as e.g. plastic and metal. In order to get round this effect, complex rinse aids are formulated which have e.g. silicone compounds and/or fluorinated compounds, as are described in US 5,880,089 or US 2005/0143280 A1. However, these compounds are biodegradable with difficulty, if at all, and some are even hazardous to the environment.

25 **[0003]** More recently, moreover, combination products have increasingly been used; these combine the different functions, such as cleaning, clear rinsing, water softening and optionally metal protection, in particular silver protection, or a glass protection function in one, preferably solid, supply form. Such compositions are referred to as multifunctional compositions. Thus, for example so-called three-in-one products which combine cleaner, rinse aid and water softener in the form of a solid compact ("tab") are found on the market. As a result of the increased use of such multifunctional compositions, however, the drying performance has become worse compared to using a classic rinse aid. Drying performance is to be understood here as meaning to what extent the cleaned ware still has water, preferably water drops, on the surface after passing through the dishwashing process. The water remaining on the surface then has to either be removed mechanically (e.g. by wiping dry) or the ware has to be left to dry in the air. The user thus has to wait until the water has evaporated. In this connection, however, residues (e.g. lime and/or surfactant residues or other residues which were dissolved or dispersed in the water) remain on the surface and lead to unaesthetic spots or streaks. This is true to a particular extent on shiny or transparent surface, such as e.g. glass or metal. For improved drying in a dishwasher, an extension or intensification of the drying phase would also in principle be conceivable, e.g. as a result of increasing the temperature in the drying step. However, not all ware withstands higher temperatures, and plastic articles in particular may be sensitive. An extension of the drying phase is in most cases perceived as a disadvantage by users.

35 **[0004]** The state of the art proposes quite a number of non-ionic surfactants as suitable additives for rinse aids in order to improve performance and reduce cycle time. For example:

- Fatty acid alkanol amide polyglycol ethers (EP 2204439 A1, COGNIS);
- Polyol alkyl ethers (EP 1607468 B1, HENKEL);
- Fatty alcohol polyglycol ethers with defined chain length and degree of alkoxylation (EP 1727884 B1, HENKEL); or
- Acrylic acid polyglycol ethers (WO 2004 013269 A1, HENKEL).

50 **[0005]** However, none of these examples fulfil the needs as explained above.

[0006] As a matter of fact, the measures as described above lead to an increased energy consumption of the machine. However, it is desired to avoid the latter since energy consumption is becoming an ever more important selling criterion for dishwashing detergents. For some time, consumers have already been paying more and more attention to the energy

consumption of domestic appliances. There are even already standards, inter alia for energy consumption and drying performance, thus e.g. the standard OEVN/OENORM EN 50242 edition 2003-11-01, valid for Austria, or the contextually similar standard for Germany, **DIN EN 50242**. Here in particular the edition 2005-06 "Electric dishwashers for household use-measurement methods for use properties" (IEC 60436:2004, modified); German version EN 50242:2004).

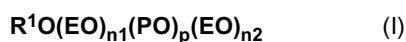
[0007] There is therefore an increased need for technical solutions for making dishwashing processes more effective and in particular more energy-saving. Such solutions may also be the use of dishwashing detergents, or additives in such compositions, which shorten the high energy-expenditure drying step, or make it possible to dry at a lower temperature, while providing the same or even better results in shorter times.

[0008] Ways are therefore sought to improve the drying performance of cleaners for hard surfaces, particular with regard to plastic and metal ware, and more particular of dishwashing detergents for automatic dishwashing, where, here, in particular those solutions are sought in which the performance in the clear-rinse cycle is increased in order to shorten time and to save energy.

DESCRIPTION OF THE INVENTION

[0009] Object of the present invention is a liquid rinse aid composition, comprising a surfactant blend comprising or consisting of

(a) a first non-ionic surfactant of formula (I)



in which

R^1 stands for a linear alkyl radical having 9 to 11 carbon atoms;

$n1$ stands for 0 or an integer of from 6 to 10;

$n2$ stands for 0 or an integer of from 6 to 10;

p stands for 0 or an integer of from 4 to 6;

and

(b) a second non-ionic surfactants of formula (II)



in which

R^2 stands for a linear alkyl radical having 10 carbon atoms;

$m1$ stands for 0 or an integer of from 6 to 10;

$m2$ stands for 0 or an integer of from 6 to 10;

q stands for 0 or an integer of from 4 to 6;

on condition that both sums $(n1+p+n2)$ and $(m1+q+m2)$ is different from 0.

[0010] Surprisingly, it has been observed that surfactants blends comprising the non-ionic surfactants of formula (I) and (II), preferably in a ratio by weight of from about 1:5 to about 5:1 provides superior results with regard to drying cycle and cleaning performance of rinse aids, preferably with regard to plastic and metal, which are the most difficult materials to rinse. The effect is demonstrated for various substrates in comparison with other non-ionic surfactants known from the state of the art for the same purpose.

SURFACTANT BLENDS

[0011] The surfactant blends as proposed by the invention represent a binary mixture of an oxoalcohol and a fatty

alcohol alkoxylated, more particularly component (a) represents an alkoxylated $C_{9/11}$ oxoalcohol of formula (I), wherein n_1 stands for 8 to 9, p stands for 5 to 6 and n_2 stands for 0. On the other hand, component (b) represents a fatty alcohol having 10 carbon atoms (or a pure synthetic decanol) of formula (II), wherein m_1 stands for 8 to 9, q stands for 5 to 6 and m_2 stands for 0.

[0012] The preparation takes place in the manner known to the person skilled in the art by reacting fatty alcohols or oxoalcohols with the alkoxides in the presence of acidic or basic catalysts. The components may show a broad or narrow homologue distribution.

[0013] The rinse aid compositions according to the present invention may contain the components (a) and (b) in a ratio by weight of about 5:1 to about 1:5 and more particular in a ratio by weight of about 2:1 to about 3:1.

CO-SURFACTANTS

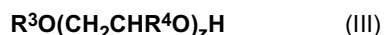
[0014] The compositions of the present invention may encompass co-surfactants (component c) different from components (a) and (b). Preferably, these co-surfactants -or emulsifiers - are of non-ionic nature, however also anionic or amphoteric surfactants are suitable.

[0015] Non-ionic surfactants. Other surfactants may also be added to the preparations as emulsifiers, including for example:

- products of the addition of 2 to 30 mol ethylene oxide and/or 0 to 5 mol propylene oxide onto linear C_{8-22} fatty alcohols, onto C_{12-22} fatty acids and onto alkyl phenols containing 8 to 15 carbon atoms in the alkyl group;
- $C_{12/18}$ fatty acid monoesters and diesters of addition products of 1 to 30 mol ethylene oxide onto glycerol;
- glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide addition products thereof;
- addition products of 15 to 60 mol ethylene oxide onto castor oil and/or hydrogenated castor oil;
- polyol esters and, in particular, polyglycerol esters such as, for example, polyglycerol polyricinoleate, polyglycerol poly-12-hydroxystearate or polyglycerol dimerate isostearate. Mixtures of compounds from several of these classes are also suitable;
- addition products of 2 to 15 mol ethylene oxide onto castor oil and/or hydrogenated castor oil;
- partial esters based on linear, branched, unsaturated or saturated $C_{6/22}$ fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, - dipentaerythritol, sugar alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example cellulose);
- mono-, di and trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates and salts thereof;
- wool wax alcohols;
- polysiloxane/polyalkyl polyether copolymers and corresponding derivatives;
- mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol and/or mixed esters of C_{6-22} fatty acids, methyl glucose and polyols, preferably glycerol or polyglycerol,
- polyalkylene glycols and
- glycerol carbonate.

[0016] Polyglycol ethers. The addition products of ethylene oxide and/or propylene oxide onto fatty alcohols, fatty acids, alkylphenols, glycerol mono- and diesters and sorbitan mono- and diesters of fatty acids or onto castor oil are known commercially available products. They are homologue mixtures of which the average degree of alkoxylation corresponds to the ratio between the quantities of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. $C_{12/18}$ fatty acid monoesters and diesters of addition products of ethylene oxide onto glycerol are known as lipid layer enhancers for cosmetic formulations.

[0017] Alkoxyated alcohols. Particular suitable are the alkoxyated alcohols. As a consequence of the preparation, alcohol alkoxyates are referred to as fatty alcohol or oxo alcohol alkoxyates and preferably conform to the formula (III),



in which R^3 is a linear or branched alkyl and/or alkenyl radical having 6 to 22 carbon atoms, R^4 is hydrogen or an alkyl radical having 1 to 3 carbon atoms and z is numbers from 1 to 50.

[0018] The fatty alcohol alkoxyates according to the formula (III) can preferably contain ethylene oxide groups, propylene oxide groups or both alkoxides, where these may be present blockwise (first one block of ethylene oxide, then one block of propylene oxide, or vice versa; or the molecule contains several blocks of different alkoxyates in succession, where a block is to be understood as meaning at least two identical alkoxide group) or in random distribution.

[0019] Partial glycerides. Typical examples of suitable partial glycerides are hydroxystearic acid monoglyceride, hydroxystearic acid diglyceride, isostearic acid monoglyceride, isostearic acid diglyceride, oleic acid monoglyceride, oleic acid diglyceride, ricinoleic acid monoglyceride, ricinoleic acid diglyceride, linoleic acid monoglyceride, linoleic acid diglyceride, linolenic acid monoglyceride, linolenic acid diglyceride, erucic acid monoglyceride, erucic acid diglyceride, tartaric acid monoglyceride, tartaric acid diglyceride, citric acid monoglyceride, citric acid diglyceride, malic acid monoglyceride, malic acid diglyceride and technical mixtures thereof which may still contain small quantities of triglyceride from the production process. Addition products of 1 to 30 and preferably 5 to 10 mol ethylene oxide onto the partial glycerides mentioned are also suitable.

[0020] Sorbitan esters. Suitable sorbitan esters are sorbitan monoisostearate, sorbitan sesquiisostearate, sorbitan diisostearate, sorbitan triisostearate, sorbitan monooleate, sorbitan sesquioleate, sorbitan dioleate, sorbitan trioleate, sorbitan monoerucate, sorbitan sesquierucate, sorbitan dierucate, sorbitan trierucate, sorbitan monoricinoleate, sorbitan sesquiricinoleate, sorbitan diricinoleate, sorbitan tricinoleate, sorbitan monohydroxystearate, sorbitan sesquihydroxystearate, sorbitan dihydroxystearate, sorbitan trihydroxystearate, sorbitan monotartrate, sorbitan sesquitartrate, sorbitan ditartrate, sorbitan tritartrate, sorbitan monocitrate, sorbitan sesquicitrate, sorbitan dicitrate, sorbitan tricitrate, sorbitan monomaleate, sorbitan sesquimaleate, sorbitan dimaleate, sorbitan trimaleate and technical mixtures thereof. Addition products of 1 to 30 and preferably 5 to 10 mol ethylene oxide onto the sorbitan esters mentioned are also suitable.

[0021] Polyglycerol esters. Typical examples of suitable polyglycerol esters are Polyglyceryl-2 Dipolyhydroxystearate (Dehymuls® PGPH), Polyglycerin-3-Diisostearate (Lameform® TGI), Polyglyceryl-4 Isostearate (Isolan GI 34), Polyglyceryl-3 Oleate, Diisostearoyl Polyglyceryl-3 Diisostearate (Isolan® PDI), Polyglyceryl-3 Methylglucose Distearate (Tego Care 450), Polyglyceryl-3 Beeswax (Cera Bellina®), Polyglyceryl-4 Caprate (Polyglycerol Caprate T2010/90), Polyglyceryl-3 Cetyl Ether (Chimexane® NL), Polyglyceryl-3 Distearate (Cremophor® GS 32) and Polyglyceryl Polyricinoleate (Admul® WOL 1403), Polyglyceryl Dimerate Isostearate and mixtures thereof. Examples of other suitable polyolesters are the mono-, di- and triesters of trimethylol propane or pentaerythritol with lauric acid, cocofatty acid, tallow fatty acid, palmitic acid, stearic acid, oleic acid, behenic acid and the like optionally reacted with 1 to 30 mol ethylene oxide.

[0022] Anionic surfactants. Typical anionic emulsifiers are aliphatic C_{12-22} fatty acids, such as palmitic acid, stearic acid or behenic acid for example, and C_{12-22} dicarboxylic acids, such as azelaic acid or sebacic acid for example. Further suitable anionic surfactants are also the salts of alkyl esters of phosphoric acid, preferably the mono- or dialkyl esters, where the alkyl radicals preferably have 6 to 12 and in particular 8 to 12 carbon atoms.

[0023] Amphoteric surfactants. Other suitable emulsifiers are amphoteric or zwitterionic surfactants. Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as the N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example coco-acylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known under the CTFA name of *Cocamidopropyl Betaine* is particularly preferred. Ampholytic surfactants are also suitable emulsifiers. Ampholytic surfactants are surface-active compounds which, in addition to a $\text{C}_{8/18}$ alkyl or acyl group, contain at least one free amino group and at least one $-\text{COOH}-$ or $-\text{SO}_3\text{H}-$ group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethyl aminopropionate and $\text{C}_{12/18}$ acyl sarcosine.

HYDROTROPES

[0024] As a further component, the rinse-aid compositions comprise a hydrotrope (component d). Hydrotropes are

agents which act as solubility promoter for a second, more sparingly soluble substance.

[0025] The preferred hydrotropes are selected from the group of cumene sulfonates, xylene sulfonates, propylene glycols and their mixtures, and here preferably 1,2-monopropylene glycol, preference being given to cumene- and xylene sulfonates.

[0026] Cumene- and xylene sulfonates are to be regarded as particularly preferred component (d), here in particular the sodium salts of cumene- or xylene sulfonate. Particular preference is given to cumene sulfonate, sodium salt.

ORGANIC ACIDS

[0027] As another optional component (e), the rinse aids according to the invention may comprise an organic acid and here usually organic hydroxycarboxylic acids which are preferably selected from the group mandelic acid, lactic acid, hydroxysuccinic acid, citric acid, tartaric acid and their mixtures, with particular preference being given to citric acid.

RINSE AID COMPOSITIONS

[0028] The rinse aid compositions of the present invention may further comprise non-ionic surfactants different from components (a) and (b), cumene sulfonate and/or citric acid.

[0029] In particular such composition may encompass

(a) about 5 to about 15 % b.w. surfactant of formula (I);

(b) about 1 to about 5 % b.w. surfactant of formula (II);

(c) 0 or about 1 to 5 % b.w. co-surfactants;

(d) 0 or about 1 to about 15 % b.w. hydrotropes;

(e) 0 or about 1 to about 5 % b.w. organic acids,

on condition that the amounts add with water and optionally usual auxiliary agents to 100 % b.w.

[0030] The compositions of the present invention can also comprise polymers, although it may be preferred for the compositions to be free from polymers, in particular free from polymers which comprise poly(meth)acrylic acid monomers.

[0031] The compositions are prepared by mixing the different components, optionally with the input of energy by stirring and/or heating of the mixtures. Preferably, after introducing the water as initial charge, the remaining components are added in any order with stirring and then the mixture is further stirred until clear.

[0032] Besides the essential components a) to c) and water, further ingredients that are customary per se may also be present in the rinse aids according to the invention. These are preferably selected from the group of alcohols and here preferably the short-chain alcohols ethanol, propanol, isopropanol, butanol, isobutanol. Moreover, the compositions can also comprise further additives, such as e.g. alkylpyrrolidones, polymers, e.g. polycarboxylates or preservatives, e.g. isothiazolinones.

[0033] The compositions can, however, also comprise perfumes, dyes, UV protection, e.g. benzophenones, pH regulators and further customary additives, e.g. those for preventing glass or metal corrosion and for protecting metals against tarnishing. The pH of the compositions can be in the range from pH 3 to 10, preferably from pH 3.5 to 8 and particularly preferably from 4 to 7 or 4 to 6. It is generally the case that acidic compositions (pH<7) may be preferred.

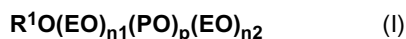
[0034] However, preference is given to those aqueous compositions which comprise only the components (a) to (e). Furthermore, it may be advantageous to dispense with the presence of hydrocarbons and in particular terpenes. In one preferred embodiment of the invention, the compositions are therefore free from terpenes and/or hydrocarbons.

[0035] The present application further provides the use of compounds of the general formula (I) according to claim for producing aqueous rinse aids, or for producing dishwashing detergents. Particular preference is moreover given to the use of compounds of the general formula (I) according to the above description for improving the drying performance of rinse aids for dishwashing, or of dishwashing detergents.

SURFACTANT BLENDS

[0036] Another object of the present invention relates to a surfactant blend consisting of

(a) a first non-ionic surfactant of formula (I)



in which

- R^1 stands for a linear alkyl radical having 9 to 11 carbon atoms;
 $n1$ stands for 0 or an integer of from 6 to 10;
 $n2$ stands for 0 or an integer of from 6 to 10;
 p stands for 0 or an integer of from 4 to 6;

and

(b) a second non-ionic surfactants of formula (II)



in which

- R^2 stands for a linear alkyl radical having 10 carbon atoms;
 $m1$ stands for 0 or an integer of from 6 to 10;
 $m2$ stands for 0 or an integer of from 6 to 10;
 q stands for 0 or an integer of from 4 to 6;

on condition that both sums $(n1+p+n2)$ and $(m1+q+m2)$ is different from 0.

[0037] Preferably the components (a) and (b) are present in said blend in a ratio by weight of from about 1:5 to about 5:1, and preferably about 2:1 to 3:1.

[0038] The surfactant blends according to formulae (I) and (II) can be incorporated into customary rinse aids and in particular dishwashing detergents on their own or in combination with the components (c) to (e). The dishwashing detergents may be solid, or in pressed form, e.g. as a tablet, or be liquid or gel-like. The compounds of the formula (I) are present in ready-formulated dishwashing detergents preferably in amounts of from 1 to 45 percent by weight, in particular in amounts of from 4 to 30 percent by weight and particularly preferably in amounts of from 15 to 30 percent by weight.

[0039] Such ready-formulated, thus standard commercial dishwashing detergents comprise e.g. builder materials, surfactants, bleaches, bleach activators, enzymes, enzyme stabilizers, corrosion inhibitors, film inhibitors, complexing agents, inorganic salts, graying inhibitors, foam inhibitors, silicone oils, soil release compounds, colour transfer inhibitors, salts of polyphosphonic acids, optical brighteners, fluorescent agents, disinfectants, fragrances, dyes, antistatics, ironing auxiliaries, phobicization and impregnation agents, swelling and nonslip agents, UV absorbers, pH regulators, or a mixture thereof.

[0040] Typical formulations of such compositions for machine dishwashing comprise pentasodium triphosphate (s. sodium phosphates) in amounts of 0, or 1 to 50 percent by weight. Sodium citrate in amounts of from 30 to 45 percent by weight, sodium polycarboxylate in amounts of from 5 to 8 percent by weight, sodium metasilicate in amounts of from 10 to 60 percent by weight, 0 sodium hydrogen carbonate in amounts of from 10 to 25 percent by weight, sodium disilicate in amounts of from 10 to 30 percent by weight, sodium perborate in amounts of from 5 to 10 percent by weight, bleach activators in amounts of from 2 to 4 percent by weight, enzymes, preferably protease and amylase, in amounts of from 1 to 6 percent by weight, low-foam non-ionic surfactants in amounts of from 1 to 20 percent by weight, silver/glass protection and fragrances in amounts up to 5 percent by weight. Suitable surfactants are anionic, non-ionic, cationic and/or amphoteric surfactants, where non-ionic surfactants and here low-foam non-ionic surfactants may be particularly preferred. The latter are preferably selected from the class of fatty alcohol alkoxylate, preferably the fatty alcohol ethoxylates, where end-group-capped derivatives may also be suitable.

INDUSTRIAL APPLICATION

[0041] The surfactant blends of formulae (I) and (II) show, alone or preferably in combination with hydrotropes (d) in rinse aids or in dishwashing detergents during automatic dishwashing, an improved drying behaviour on porcelain, glass, metal and plastic (e.g. in the case of Tupperware, SAN (=styreneacrylonitrile), melamine, polypropylene, polyethylene). The improved drying performance on plastic and metal substrates is particularly well pronounced. The improved drying behaviour is moreover more pronounced when using low-temperature programmes or saving or eco programmes with a reduced maximum temperature in the clear-rinse cycle and/or in the drying step. In one preferred embodiment, the compounds of the formula (I) are used rinse aids or dishwashing detergents as additives which serve to improve the

drying performance and/or the cleaning performance. The surfactant blends can be used here either in aqueous compositions, preferably in aqueous rinse aids, or else in solid compositions. In general, the surfactant blends are suitable for producing rinse aids or dishwashing detergents.

[0042] The present application therefore further provides a method for rinsing a hard surface in an automatic dishwashing machine, wherein said surfaces are brought into contact with the rinse aid composition or the surfactant blend of the invention. More particularly, the present invention encompasses a method for automatic dishwashing, where the ware passes through at least one cleaning cycle using a detergent and water, at least one clear-rinse cycle using a rinse aid and water, and a final drying cycle, where the temperature in the drying cycle does not exceed 50 °C, where a surfactant blend as per the above description is used. By using surfactant blend in a rinse aid composition as defined above, cleaning performance is improved and the drying temperatures can be reduced from the 70 to 60 °C otherwise customary in such processes to 55 °C or even lower, e.g. down to 45 or 50 °C.

[0043] Another object of the present invention is related to use of the surfactant blend as defined above for making liquid rinsing aids. As explained above, the use of the surfactant blends of the present invention in dishwashing detergents and/or in rinse aids thus permits both a notable improve in performance and a saving of energy compared with current dishwashing processes and compositions since, on account of the improved drying behaviour, a shorter drying time or preferably a lower drying temperature, preferably less than 60 degrees centigrade and in particular from 40 to 59 °C, very particularly preferably from 45 to 55 °C, can be used. The washing process according to the above description is suitable for meeting the requirements placed on drying performance and energy consumption according to the German standard DIN EN 50242.

[0044] Finally, another object of the present invention is related to the use of the liquid rinse aids for making solid dishwashing agents, such as for example powders, tablets, granules, extrudates and the like.

EXAMPLES

Examples 1 and 2, Comparative Examples C1 to C6

[0045] The following Table 1 shows the exceptional performance of the compositions comprising the surfactant mixture according to the invention on plastic and metal wares. The following graphic shows the exceptional performance of the new invention on plastic. All the formulations have exactly the same frame formulation with the non-ionic surfactant active amount (w/w) being 14%. They differ only in non-ionic surfactant types.

[0046] The test method is defined by **wfk institute**. Rinse aid performance is tested with an automatic dish washing machine of Miele G 1222 SC type over 3 rinse cycles, using Universal 55 °C programme with prewash. Water hardness is 8-10 °d. The test compositions were placed in the dish washer with 50 g soil. 20 g automatic dishwasher cleaner was dosed at the beginning of washing process and 5 mL of rinse aid is dosed at the beginning of the rinse cycle.

Substrates tested:

[0047] Substrates tested:

- Porcelain plate
- 3 different types of glass: potassic crystal glass, crystalline glass, soda lime glass
- Stainless steel knives
- Plastic bowls made of polypropylene

[0048] A visual assessment described in Tenside Surf. Det. 28 (1991) 5 is used to determine the performance of all the dishware. The results are shown in **Table 1** and represent median values over 3 trials for plastic and steel respectively.

Table 1 Performance of rinse aid compositions on plastic and steel

Examples	1	2	C1	C2	C3	C4	C5	C6
C _{9/11} +8.5EO+5.5PO	10.0	4.0	4.0	4.0	4.0	4.0	-	-
C ₁₀ +8.5EO+5.5PO	4.0	10.0	-	-	-	-	4.0	4.0
C _{13/15} +9EO+1BO	-	-	10.0	-	-	-	-	-

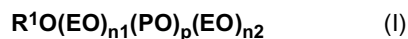
(continued)

Examples	1	2	C1	C2	C3	C4	C5	C6
C _{12/15} +6EO+3PO	-	-	-	10.0	-	-	10.0	-
C _{12/14} +4EO+5PO	-	-	-	-	10.0	-	-	-
C _{12/15} +6EO+4PO	-	-	-	-	-	10.0	-	10.0
Polyglycol butylether	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Cumene sulfonate	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Citric acid	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Preservative	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water	Ad 100							
Performance Plastic								
Stripes and spots	4	2	1	1	1	1	1	3
Film	3	3	3	3	2	2	2	2
Performance Steel								
Stripes and spots	4	4	2	3	2	2	2	4
Film	3	2	2	2	1	2	1	3

Claims

1. A liquid rinse aid composition, comprising a surfactant blend comprising or consisting of

(a) a first non-ionic surfactant of formula (I)



in which

R¹ stands for a linear alkyl radical having 9 to 11 carbon atoms;

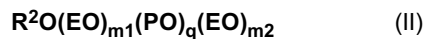
n₁ stands for 0 or an integer of from 6 to 10;

n₂ stands for 0 or an integer of from 6 to 10;

p stands for 0 or an integer of from 4 to 6;

and

(b) a second non-ionic surfactants of formula (II)



in which

R² stands for a linear alkyl radical having 10 carbon atoms;

m₁ stands for 0 or an integer of from 6 to 10;

m₂ stands for 0 or an integer of from 6 to 10;

q stands for 0 or an integer of from 4 to 6;

on condition that both sums (n₁+p+n₂) and (m₁+q+m₂) is different from 0.

2. The composition of Claim 1, wherein n₁ stands for 8 to 9, p stands for 5 to 6 and n₂ stands for 0.

3. The composition of Claim 1, wherein m₁ stands for 8 to 9; q stands for 5 to 6 and m₂ stands for 0.

4. The composition of Claim 1, wherein the components (a) and (b) are present in a ratio by weight of about 5:1 to about 1:5.
5. The composition of Claim 1, wherein the components (a) and (b) are present in a ratio by weight of about 2:1 to about 3:1.
6. The composition of Claim 1, further comprising co-surfactants different from components (a) and (b), hydrotropes and/or organic acids.
7. The composition of Claim 6, wherein said co-surfactants (component c) are selected from the group consisting of non-ionic surfactants.
8. The composition of Claim 6, wherein said hydrotropes (component d) are selected from the group consisting of cumene sulfonates, xylene sulfonates, propylene glycols and their mixtures.
9. The composition of Claim 6, wherein said organic acids (component e) are selected from the group consisting of mandelic acid, lactic acid, hydroxysuccinic acid, citric acid tartaric acid, and their mixtures.
10. The composition of Claim 1, further comprising non-ionic surfactants different from components (a) and (b), cumene sulfonate and/or citric acid.

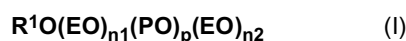
11. The composition of Claim 1, comprising

- (a) about 5 to about 15 % b.w. surfactant of formula (I);
- (b) about 1 to about 5 % b.w. surfactant of formula (II);
- (c) 0 or 1 to 5 % b.w. co-surfactants;
- (d) 0 or about 1 to about 15 % b.w. hydrotropes;
- (e) 0 or about 1 to about 5 % b.w. organic acids,

on condition that the amounts add with water and optionally usual auxiliary agents to 100 % b.w.

12. A surfactant blend consisting of

- (a) a first non-ionic surfactant of formula (I)



in which

- R¹ stands for a linear alkyl radical having 9 to 11 carbon atoms;
- n₁ stands for 0 or an integer of from 6 to 10;
- n₂ stands for 0 or an integer of from 6 to 10;
- p stands for 0 or an integer of from 4 to 6;

and

- (b) a second non-ionic surfactants of formula (II)



in which

- R² stands for a linear alkyl radical having 10 carbon atoms;
- m₁ stands for 0 or an integer of from 6 to 10;
- m₂ stands for 0 or an integer of from 6 to 10;
- q stands for 0 or an integer of from 4 to 6;

on condition that both sums (n₁+p+n₂) and (m₁+q+m₂) is different from 0.

EP 2 963 100 A1

13. A method for rinsing a hard surface in an automatic dishwashing machine, wherein said surfaces are brought into contact with the composition of Claim 1 or the surfactant blend of Claim 12.

14. The use of the surfactant blend of Claim 12 for making liquid rinsing aids.

15. The use of the liquid rinsing aids of Claim 1 for making solid dishwashing agents.

5

10

15

20

25

30

35

40

45

50

55



EUROPEAN SEARCH REPORT

Application Number
EP 14 17 5880

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 023 431 A1 (PROCTER & GAMBLE [US]) 2 August 2000 (2000-08-02)	1,4-10	INV. C11D1/825
A	* claims; examples *	2,3, 11-15	C11D1/72 C11D1/722

X	WO 94/12600 A1 (PROCTER & GAMBLE [US]) 9 June 1994 (1994-06-09)	1,4-10	
A	* page 6, lines 5-12; claims; examples *	2,3, 11-15	

A	WO 2014/095793 A1 (AKZO NOBEL CHEMICALS INT BV [NL]) 26 June 2014 (2014-06-26)	1-15	
	* page 1, lines 5-8; claims; examples *		

A	US 5 273 677 A (ARIF SHOAI B [US]) 28 December 1993 (1993-12-28)	1-15	
	* column 3, lines 4-31; claims; examples *		

A	WO 92/14808 A1 (BASF AG [DE]) 3 September 1992 (1992-09-03)	1-15	
	* page 5, lines 1-5; claims; examples *		

The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
			C11D
Place of search		Date of completion of the search	Examiner
Munich		13 January 2015	Péntek, Eric
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 03.92 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 14 17 5880

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-01-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1023431 A1	02-08-2000	AT 284943 T	15-01-2005
		BR 9813070 A	16-10-2001
		DE 69828192 D1	20-01-2005
		DE 69828192 T2	22-12-2005
		EP 1023431 A1	02-08-2000
		ES 2235373 T3	01-07-2005
		JP 2001520269 A	30-10-2001
		WO 9919449 A1	22-04-1999
WO 9412600 A1	09-06-1994	AU 670374 B2	11-07-1996
		CA 2148810 A1	09-06-1994
		EP 0598973 A1	01-06-1994
		EP 0670876 A1	13-09-1995
		FI 952539 A	24-05-1995
		JP H08503731 A	23-04-1996
		NO 952057 A	24-05-1995
		NZ 278814 A	27-05-1998
		RU 95113462 A	20-03-1997
		WO 9412600 A1	09-06-1994
WO 2014095793 A1	26-06-2014	NONE	
US 5273677 A	28-12-1993	NONE	
WO 9214808 A1	03-09-1992	AT 127150 T	15-09-1995
		CA 2104468 A1	23-08-1992
		DE 4105602 A1	27-08-1992
		DK 0572453 T3	18-09-1995
		EP 0572453 A1	08-12-1993
		JP H06505044 A	09-06-1994
		US 5536884 A	16-07-1996
		WO 9214808 A1	03-09-1992

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5880089 A [0002]
- US 20050143280 A1 [0002]
- EP 2204439 A1 [0004]
- EP 1607468 B1 [0004]
- EP 1727884 B1 [0004]
- WO 2004013269 A1 [0004]

Non-patent literature cited in the description

- OEVI/OENORM EN, 01 November 2003 [0006]
- *Tenside Surf. Det.*, 1991, vol. 28, 5 [0048]