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(54) **Mixture of a surfactant with a solid compound for improving rinsing performance of automatic dishwashing detergents**

Mischung aus einem Tensid mit einer Festverbindung zur Verbesserung der Spülleistung von automatischen Geschirrspülmitteln

Mélange d'un agent tensioactif avec un composé solide pour améliorer la performance de rinçage de détergents pour le lavage automatique de la vaisselle

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• **Van Ommen, Janco**

8031 EZ Zwolle (NL)

• **Schuldink, Henk**

7772 KH Hardenberg (NL)

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(74) Representative: **f & e patent**

Fleischer, Engels & Partner mbB, Patentanwälte

Braunsberger Feld 29

51429 Bergisch Gladbach (DE)

(73) Proprietor: **Dalli-Werke GmbH & Co. KG**
52224 Stolberg (DE)

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Description

[0001] The present invention refers to a rinse aid additive comprising more than 40 wt.-% based on the total weight of the rinse aid additive of a surfactant possessing a dynamic viscosity of equal or greater than 10^5 mPa·s at a temperature of 20 °C, which drops in the temperature interval of between above 20 °C to about 40 °C by a factor of 25 per 10°C or more, and a solid compound, wherein said rinse aid additive is in form of a solid at room temperature, a method for preparing said rinse aid additive, a detergent composition comprising said rinse aid additive and the use of a blend comprising at least a surfactant and a solid compound as a rinse aid.

[0002] Domestic automatic dishwasher detergents commonly are used in combination with a "softening" salt and a rinse aid compound. The ion exchanger in the dishwashing-machine uses the "softening" salt to soften the water used during the whole program so the hardness doesn't exceed certain limits and a deposit of lime scale is preferably low. In prior art the dishwashing machine dosed the detergent composition at the time point the detergent was needed in the cleaning process and the rinse aid when it was needed during the rinsing phase of the program.

[0003] The user had to be sure that at the moment the program was started the amount of detergent composition, rinse aid and softening salt in the dishwasher was sufficient in order to get an optimal overall cleaning result.

[0004] From a convenience point-of-view the detergent producers introduced more-in-one products on the market. More-in-one products include the water softening function of the salt as well as the ion exchanger and the function of the rinse aid thus the desired cleaning performance of the detergent composition is realized in one detergent product.

[0005] These more-in-one products have certain limits. To obtain an optimal cleaning result the maximum hardness of the used tap-water should not exceed 21°GH. In cases where the used tap water exceeds this limit it is still advised to keep using the softening salt beside the more-in-one detergent in the dishwasher. When the consumer is not satisfied with the shine and appearance of the cleaned machine load additional rinse aid can be used.

With a more-in-one detergent composition the softening salt function, the cleaning function and the rinse-aid function all are supplied at the moment when the detergent composition is dosed. This renders the performance difficult because the detergent, the softening function and the rinse aid function are needed at different time points/periods during the cleaning program of the dishwashing machine.

Known techniques to solve this problem are based on affecting the dissolution or disintegration of the detergent or of one or several particular ingredient(s). Some of the options known in the art for affecting the dissolution or disintegration of ingredients or at least a part of the detergent composition are based on e.g. the physical shape of the detergent composition or ingredient, the porosity of the ingredients or use of compressed ingredients or powder form of the detergent composition or ingredient, helping aids for accelerating or decelerating dissolution or disintegration, melting temperature of ingredients, pH of washing liquid, coating of ingredients or detergents, etc.

Known in the art are furthermore so-called carry-over surfactants. These are well described in EP-A 1 524 313.

[0006] Automatic dishwashing detergent tablet containing non-compressed portion called rinse additive comprising a hot melt surfactant which is solid at ambient temperature and melts in a temperature range from 35°C to 150°C in combination with sodium citrate, PEG200 and dye is disclosed in EP2071018.

[0007] It was an object of the present invention to provide an additive which allows an increased cleaning performance, in particular an increased spotting and/or preferably increased filming performance resulting in a satisfying shine and appearance of the cleaned tableware. E.g. when having a spotting performance comparable to known rinse aid additives the filming performance of the additive of the present invention should be superior or vice versa.

[0008] This object is met by a rinse aid additive for automatic dishwashing provided in form of a

- (i) non-compressed part attached to a compressed detergent composition, or
- (ii) non-compressed part separate of a compressed or non-compressed detergent composition in any shape that can be dosed separate from a detergent, or
- (iii) granulate that is contained in a compressed or non-compressed detergent composition.

comprising more than 40 wt.-% based on the total weight of the rinse aid additive of surfactant, possessing a dynamic viscosity of equal or greater than 10^5 mPa·s at a temperature of 20 °C, which drops in the temperature interval of between above 20 °C to about 40 °C by a factor of 25 per 10°C or more, and at least one solid compound, wherein said rinse aid additive is in form of a solid at room temperature.

[0009] According to this invention surprisingly it was found that the use of a mixture of at least one surfactant, which is semi-solid at room temperature (defined by its dynamic viscosity as above), with at least one solid compound in combination with an automatic dishwasher detergent composition results in an improved rinse-aid performance of the detergent composition or an improved drying performance of the detergent composition or both.

[0010] The mixture preferably should be solid at temperatures below 30 °C and become waxy at temperatures of 35

°C or higher.

[0011] In terms the present invention the term "solid" refers to a continuous mass of a compound or a composition. A solid has a stable, definite shape, and a definite volume and changes its shape only by force or energy, as when broken, cut, or melted. In this respect it should be understood that for instance a granulate or a powder is composed of a plurality of solid particles, but as a whole does not represent a continuous solid mass.

[0012] The surfactant used in the mixture is at least one of that which is known to give a dishwasher detergent composition a positive effect on the rinse aid performance and the drying performance. The term "semi-solid at room temperature" means that at a temperature of 20 °C or less the surfactant preferably has a dynamic viscosity of equal to or greater than 10⁵ mPa·s (10² N·s·m⁻²). At 20 °C, the surfactant may for example be pasty, i.e., in the form of a suspension of solid material in a background fluid.

[0013] At higher temperatures the surfactant becomes more waxy or liquid and less solid and the dynamic viscosity drops. Particularly preferred are surfactants which at a temperature of 20 °C or less have a dynamic viscosity of greater than 10⁵ mPa·s (10² N·s·m⁻²), which significantly drops in the temperature interval of between above 20 °C to about 40 °C, preferably in the temperature interval between above 20 °C to about 30 °C for instance by a factor of 25 per 10 °C or more. The dynamic viscosity at 30 °C may for example be as low as about 4.000 mPa·s (4 N·s·m⁻²) or even lower.

[0014] Preferred surfactants are a fatty alcohol ethoxylate, a fatty acid ethoxylate or a mixture of several of such surfactants. It is particularly preferred that said surfactant(s) have independently a carbon chain from averagely 11 to averagely 22 carbon atoms and from averagely 5 to averagely 150 (inclusive) ethylene oxide groups. With "averagely" is meant that the provided ethoxylates can have carbon chains and/or ethylene oxide groups of different chain length or in different amounts, respectively, however, in average the length/amount defined before is obtained. The carbon chain can be linear or branched and saturated, mono- or poly-unsaturated. In terms of the present invention the term "ethoxylated" surfactant preferably only comprises surfactants comprising -(CH₂CH₂O)-EO groups, but not surfactants comprising mixed alkoxyated chains or block copolymers, i.e. surfactants also containing further alkoxyate groups other than ethoxylate groups, such as for instance propoxylate groups. With "inclusive" is meant that the surfactant may comprise any number of ethylene oxides groups from averagely 5 to averagely 150, e.g. averagely 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130 and 140.

[0015] Another preferred surfactant is a so-called Gemini surfactant comprising an ethoxylated spacer or a mixture of several of such surfactants. Gemini surfactants consist of two "usual" surfactant molecules, i.e. both usually comprising a terminal hydrocarbon tail and a polar head group, e.g. fatty alcohols or fatty acids covalently linked by a spacer group. It is particularly preferred that said surfactant(s) has/have tails of hydrocarbon chains comprising from averagely 6 to averagely 18 carbon atoms per tail and as a spacer bridging the two carbon chains a poly(ethylene oxide chain) -(EO)_n-, wherein n ranges from averagely 4 to averagely 80 ethylene oxide groups, per Gemini surfactant molecule.

[0016] A mixture of the preferred surfactants described above can also be used, e.g. a mixture of one or more fatty alcohol ethoxylate(s) and one or more ethoxylated Gemini surfactants described above.

[0017] Examples are the surfactants, available as Lutensol TO range (BASF) with an average of 10 to 40 (inclusive) ethylene oxide groups, Lutensol AT range (BASF) and the Genapol T range (Clariant), both with an average of 5 to 80 (inclusive) ethylene oxide groups, including e.g. 10, 20, 30, 40, 50, 60, and 70 ethylene oxide groups, and products like Emulan AF, and Emulan AT9 (BASF) and the surfactants of the Imbentin series like Imbentin-AG/124S/110 and -AG/124S/180, -AG/128S/100, -AG/168S/60 to -AG/168S/800 G, -POA/050 5055 to -POA/800G, -AG/124H/070, -AG/124/150, -AG/200/120, -T/65 to -T/400 G, -C/135/090 to -C/125/200, -C/145/050 to -C/145/130 and Hedin-PS/060, -PS/090 and -PS/400 G (Dr Kolb) and Dehypón GRA and Dehypón E127 (Cognis).

[0018] Preferably the surfactant(s) may have a molecular weight of from about 400 to 1,000 g/mol, more preferably about 500 to about 800 g/mol. The surfactants present in the rinse aid preferably may have a surface tension of about 32 - 43 mN/m, measured according to DIN 53914 at a concentration of 1 g/L (distilled water), applying Harkins-Jordan correction. Preferably its HLB value (hydrophilic-lipophilic balance) may be above 8, more preferably in the range of from about 9 to about 15.

[0019] The surfactant's cloud point preferably may be above 50 °C, more preferably above 55 °C and even more preferably above 60 °C, as determined in water according to DIN 53917.

[0020] The pH of a solution of the surfactant in water (5 wt-%) preferably may have an (almost) neutral pH, i.e. a pH of about 7.

[0021] Preferably the solubility of the surfactant in distilled water may be below 10 % (w/w) at 23 °C. Preferably the solubility of the surfactant in potable water may be below 10 % (w/w) at 23 °C. Preferably the solubility of the surfactant in 5 % NaOH (aq) may be below 10 % (w/w) at 23 °C. Preferably the solubility of the surfactant in 5 % HCl (aq) may be below 10 % (w/w) at 23 °C. Preferably the solubility of the surfactant in 5 % saline solution may be below 10 % (w/w) at 23 °C.

[0022] The solid compound can be any preferably particulate ingredient that blends well with the semi-solid surfactant at elevated temperatures resulting in a liquid or waxy mixture / suspension at said elevated temperature and provides a stable solid at room temperature.

[0023] With elevated temperature is meant a temperature between 35 °C and 250 °C.

[0024] When the blend comprising at least the (semi-solid) surfactant and the solid compound is combined with a detergent composition, the rinsing and drying performance of the detergent or both are improved. In particular the effect of the (semi-solid) surfactant providing the rinsing and/or drying performance is improved, when the surfactant is combined with the solid compound compared to the surfactant effect alone. Examples for suitable solid compounds are a water soluble salt, a water insoluble salt, a silicate, a silicate comprising composition, a hydrophobic or a hydrophilic polymer or a hydrophobic compound, without being limited to these.

[0025] The solid compound can be any solid not negatively intervening with the cleaning effect, preferably any of the solid ingredients suitable in detergent compositions. Examples are organic natural thickeners, organic modified natural thickeners, organic fully synthetic thickeners and inorganic thickeners known in the art, e.g. gums like for example guar gum.

[0026] Examples of the preferred solid compounds include salts, like silver, barium, calcium, zinc, titanium, zirconium, iron, aluminum, magnesium, potassium or sodium salts of chloride, sulfate, carbonate, bicarbonate, oxides, acetate, e.g. sodium carbonate, sodium chloride, zinc oxide, or zeolites (like e.g. Valfor 100 Zeolite Na A by PQ Cooperation), aluminosilicates (like Tixolex by Rhodia), fumed silicas (like Aerosil by Evonik), waxes, homo-, co- or ter-polymers of olefins, acrylic, methacrylic or maleic acids optionally further functionalized by sulfonated groups, or salts thereof, polyethylene glycol having a molecular weight of above 7000 (like Pluriol E by BASF), polysaccharides, in particular gums, for instance guar-gum (like Jaguar HP120 by Harke Chemicals), or xanthan-gum, alginate, carboxymethyl cellulose, several starch types, collagen, gelatine, tapioca, citrate or tripolyphosphate in the form of a potassium or sodium salt, citric acid, tetraacetylene diamine, benzotriazole or mixtures thereof, without being limited to these.

[0027] Said solid ingredient(s) preferably is/are provided in particulate form, e.g. like powder, granules, spheres, crystals, cubes, or any other suitable form, wherein the particles preferably have a particle size in the range of 0.1 micrometer to 2 milimeters with respect to the average diameter of the particles as determined at position of their greatest extent.

[0028] The rinse aid additive can be prepared by combining the solid compound at least with the surfactant, optionally heating the mixture to a temperature above the temperature where the surfactant becomes waxy or at least partially liquid, blending the solid at least with the surfactant and allowing the blend to cool to a temperature where the blend becomes solid.

[0029] The solid as well as the mixture may be or form a crystalline or an amorphous solid, including a "solidified melt" or a so-called "supercooled melt", i.e. a glassy substance.

[0030] For preparing the mixture of the at least one surfactant and the at least one solid according to the present invention, preferably one or more surfactants and one or more solid compounds should be blended to form a homogeneous mixture. This may be achieved by heating the surfactant(s) to a temperature in the range of between 35 °C and 200 °C, where the surfactant(s) become(s) liquid. The solid ingredient(s) preferably is/are added under constant mechanical action. When required the solid ingredient(s) can be added after being heated up to a desired temperature. The mixture is being mixed until it is homogeneous. The temperature of the mixture can be adapted to a proper temperature for processing further.

[0031] The mixture can be processed to a granulate, casted in a mould, or sprayed, casted or dosed on a detergent body. After the mixture has cooled down to a temperature below 35 °C, preferably below 30 °C, it becomes solid.

[0032] The blend comprising at least the surfactant and the solid compound preferably is combined with any detergent composition, preferably a detergent composition for automatic dishwashing. Any of the commonly known automatic dishwashing detergent compositions can be used according to the present invention, preferably any of the automatic dishwashing compositions usually used in combinations with a rinse aid compound or additive. Ingredients of such preferred automatic dishwashing compositions are shown in detail below. The detergent composition can be provided in form a powder, granulates, a tablet, a bar, a liquid or any other suitable form or combinations thereof.

[0033] The rinse aid additive of the present invention preferably is combined with such a detergent composition. The rinse aid additive is provided in form of a

- (i) non-compressed part attached to a compressed detergent composition, or
- (ii) non-compressed part separate of a compressed or non-compressed detergent composition in any shape that can be dosed separate from a detergent, or
- (iii) granulate that is contained in a compressed or non-compressed detergent composition.

[0034] The non-compressed part of the rinse aid additive according to (i) might be provided as pearls, droplets, pellets, at least one ball, stripe(s), dot(s), strand(s), extruded line(s), or a pattern in or on the compressed portion of the detergent composition or as a coating on or around at least a part of the surface of the compressed portion or non-compressed part of the rinse aid additive. The non-compressed part of the rinse aid additive according to (ii) might be provided as a powder, pearls, droplets, granulate, spheres, pellets, tablet(s), ball(s) or cube(s).

FURTHER INGREDIENTS

[0035] The following further ingredients can be included into the rinse aid additive of the present invention, or can be ingredients of a detergent composition preferably combined with the rinse aid additive of the present invention. The ingredients below can be combined in any suitably manner, e.g. some of them might be included in the blend of the rinse aid additive, while some of them might be part of the detergent composition or several of them might be included in a detergent composition, while the rinse aid additive doesn't comprise any further ingredient.

[0036] Preferably, the rinse aid additive of the present invention is provided in combination with a detergent composition, more preferably a detergent composition as described in detail below, particularly preferably a compressed detergent composition. If the rinse aid additive is combined with a detergent composition, the ratio of rinse aid additive to detergent composition preferably is in the range of from 1:5 to 1:150, more preferably of from 1:7 to 1:100, and most preferably of from 1:25 to 1:50.

[0037] In a particular preferred embodiment the amount of semi-solid surfactant in the rinse aid additives is higher than 15 wt.-%, more preferably higher than 30 wt.-%, even more preferably higher than 40 wt.-% and most preferably higher than 50 wt.-%, based on the whole rinse aid additive. The rinse aid additives may as well only consist of one or more semi-solid surfactant(s) and one or more solids described above. The ratio of the surfactant(s) to solid(s) in the rinse aid additive preferably is in the range of from 50:1 to 1:1, more preferably of from 20:1 to 1.5:1, including 15:1, 10:1, 5:1, 4:1, 3:1, and 2:1 (w/w).

[0038] Due to the use of a semi-solid surfactant whose viscosity dramatically drops in the temperature range between 20 °C and 40 °C in combination with one of the solids described above, it is surprisingly possible to provide a rinse aid which is solid at room temperature, but nevertheless can be easily distributed at the operating temperature inside a dishwashing machine, i.e. temperatures above 35 °C, even if the surfactants comprised in said rinse aid additive are not water-soluble to a significant extent (10 % (w/w) or more at 23 °C), neither in distilled nor in potable water, nor in a 5 % saline solution, 5 % HCl (aq) or 5 % NaOH (aq). Furthermore, a high amount of a surfactant (usually at least 50 wt.-%) can be comprised in the solid rinse aid additives, while many solid rinse aid compositions known in the state of the art only comprise an ethoxylated surfactant amount in the range of up to 30 wt.-%.

[0039] The detergent composition(s) of the present invention may comprise any of the ingredients known in the art as common ingredients in automatic dishwashing compositions. Said ingredients are e.g. builders, surfactants, enzymes, dyes, perfume, polymers, complexing agents, bleaching agents, bleach activators, bleach catalysts, dispersing agents, optical brighteners, process aids and anti corrosion agents, without any restriction.

[0040] Some of the compounds listed hereafter as possible ingredients of the detergent composition(s) of the present invention may be suitable as an ingredient in the rinse aid composition as well, for example as a solid component, a surfactant and/or a further additive.

[0041] Furthermore all of the optional ingredients known in the state of the art to be effective or usable in detergent compositions might be included.

[0042] Said ingredients are not limiting the present invention.

BUILDERS

[0043] The composition of the present invention may optionally comprise one or more builder(s).

[0044] The main functions of the builders are to soften the washing water, to provide alkalinity and a buffering capacity to the washing liquid and to have an anti redeposition or dispersing function in the detergent composition. The physical properties of the detergent composition are also depending on the builders that are used.

[0045] Inorganic non-phosphate builders include, but are not limited to, phosphonates, silicates, carbonates, sulphates, citrate, and aluminosilicates.

[0046] Organic builders include, but are not limited to, a wide variety of (poly)carboxylated compounds having one or more carboxylate groups.

[0047] Phosphoric builders include, but are not limited to, various alkali metal phosphates such as tripolyphosphate, pyrophosphate, orthophosphate, etc.

[0048] Complexing agents are commonly used as co-builders to support the performance of the builders.

[0049] Builders and co-builders can generally be added to the composition in acid form, neutralized or in a partly neutralized form. When used in a partly or completely neutralized form alkali metal salts are preferred, like sodium, potassium and lithium or ammonium salts.

55 SURFACTANTS

[0050] The composition of the present invention may optionally comprise one or more surfactants in addition to the (semi-solid) surfactant described above.

[0051] The main functions of surfactants are changing the surface tension, dispersing, foam controlling and surface modification. A special type of surfactants used in automatic dishwasher detergent compositions is a 'carry-over' surfactant. A 'carry-over' surfactant has the property that some amount of the surfactant used remains in the machine after the rinsing cycles to give a performance during the final rinsing cycle and the (optional) drying phase of the whole washing cycle of the dishwashing machine. This type of surfactant is described in EP 1 524 313 in more detail.

[0052] For automatic dishwasher detergent compositions alkoxylated nonionic surfactants and Gemini surfactants are commonly used. The alkoxy groups mostly consist of ethyleneoxide, propyleneoxide and butyleneoxide or combinations thereof. Also amphoteric surfactants are known to be used in automatic dishwasher detergent compositions.

[0053] Alkyl poly glucoside surfactants can also be used in automatic dishwasher detergent compositions, preferably in a low foaming form.

[0054] Further all surfactants commonly known to be used in detergent compositions can be part of the composition, this includes all anionic, non-ionic, cationic and amphoteric surfactants known in the art. The present invention is not limited by any of the surfactants commonly used in automatic dishwashing compositions.

15 ENZYMES

[0055] The composition of the present invention may optionally comprise one or more enzymes.

[0056] Enzymes are often used to aid the removal of stains. In most cases enzymes react with the soiling and break it down into particles that have increased water solubility or are better dispersible in the washing liquid.

[0057] The enzymes that can be used in detergent compositions include, but are not limited to, proteases, amylases, lipases, cellulases, mannanase, peroxidase, oxidase, xylanase, pullulanase, glucanase, pectinase, cutinase, hemicellulases, glucoamylases, phospholipases, esterases, keratanases, reductases, phenoloxidases, lipoxygenases, ligninases, tannases, pentosanases, malanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof. These enzymes are known to the skilled artisans and can be used as a granulate and liquid in common amounts.

25 ANTI CORROSION AGENTS

[0058] The detergent composition of the present invention may optionally comprise one or more anticorrosion agents.

[0059] The main function of anticorrosion agents is to minimize the amount of material damage caused on glass and metal during automatic dishwashing.

[0060] Glass corrosion occurs because metal ions are dissolved out of the glass surface. This occurs more intensively when soft tap water is used for the cleaning. In this case the builders and complexing agents can only bind a limited amount of hardness ions from the tap water and extract than (alkaline earth) metals from that glass surface. Also of influence for glass corrosion are the washing temperature, the quality of the glassware and the duration of the cleaning program.

[0061] Glass corrosion becomes visible in white lines or white clouds on the glass surface. The glass corrosion damage can be repaired by replacing the extracted metal ion, however preferably the glassware can be protected against glass corrosion.

[0062] Metal corrosion occurs in many cases when oxide, sulphide and/or chlorides are present in the washing liquid, which normally is a mixture of tap water, soil and a detergent composition. The anions react with the metal or metal alloy surface of articles that are contained in the dishwashing machine. In the case of silver the silver salts which are formed give a discoloration of the silver metal surface which becomes visible after one or more cleaning cycles in an automatic dishwashing machine.

[0063] The occurrence of metal corrosion can be slowed down or inhibited by use of detergent ingredients that provides the metal with a protective film or ingredients forming compounds with the oxide, sulfide and/or chlorides to prevent them from reacting with the metal surface.

[0064] The protective film can be formed because the inhibitor ingredient may become insoluble on the metal or metal alloy surface, or because of adsorption to the surface by aid of free electron pairs of donor atoms (like N, S, O, P). The metals can be silver, copper, stainless steel, iron, etc.

[0065] The types of anti corrosion agents which often are used in detergent compositions or which are described in literature include, but are not limited to, triazole-based compounds (like tolyltriazole and 1,2,3-benzotriazole), polymers with an affinity to attach to glass surfaces, strong oxidizers (like permanganate), cystine (as silver-protector), silicates, organic or inorganic metal salts, or metal salts of biopolymers. The metal of these metal salts can be selected from the group aluminum, strontium, barium, titanium, zirconium, manganese, lanthanum, bismuth, zinc, wherein the latter two are most commonly applied for the prevention of glass corrosion. Further compounds to be added e.g. are manganese compounds as described e.g. in WO2005/095570.

POLYMERS

[0066] The composition of the present invention may optionally comprise one or more polymers.

[0067] The main function of polymers is the effect as a (co-)builder or dispersing agent. Dispersing agents are used to inhibit crystal growth and/or to disperse insoluble materials in the washing liquor, such as (fatty) soil, inorganic or organic salts, etc. Dispersing agents often have a polymeric character and are at least partly hydrophilic. Dispersing agents are e.g. described in particular in DE 199 34 704 A1.

[0068] The polymers that often are used in detergent compositions include, but are not limited to, homo-, co- or a terpolymers of or based on oleic monomer, acrylic acid, methacrylic acid or maleic acid, or "salts" thereof which are obtained by neutralizing the acidic moieties present in these polymers, either completely or in part. Such polymers can be combined with or can include monomers that give the polymer a special function.

[0069] These polymers often also contain monomers with various properties, like e.g. sulphonated styrene, styrene, 2-acrylamido-2-methyl propane sulphonic acid, methallyl sulphonic acid, acryl amide, etc. Such polymers are commonly known and are described e.g. in EP-A 1 363 986, EP-A 1 268 729, EP-A1 299 513 and EP-A 0 877 002.

COMPLEXING AGENTS

[0070] The composition of the present invention may optionally comprise one or more complexing agent(s).

[0071] A function of complexing agents is to capture trace metal ions like, Cu(II), Fe(II), Fe(III), Mn(II), Cd(II), Co(II), Cr(III), Hg(II), Ni(II), Pb(II), Pd(II), Zn(II). These ions can interfere with or disturb certain processes of the detergent in the washing machine, like e.g. the bleach performance. Complexing agents can also be used as co-builder or builder.

[0072] The complexing agent(s) that are known to be used in detergent compositions include, but are not limited to S,S-ethylenediamine-N,N'-disuccinic acid (S,S-EDDS), ethylenediaminetetraacetic acid (EDTA), diethylene triamine penta(methylene phosphonate) (DETPMP), nitrilotriacetic acid (NTA), ethanol diglycine (EDG), imino disuccinic acid (IDS), methylglycine diacetic acid (MGDA), diethylene triamine pentaacetic acid (DTPA), ethylene diamine dihydroxy-phenyl acetic acid (EDDHA), N-(hydroxyethyl) ethylenediamine triacetic acid (HEDTA), hydroxyethylidene-1,1-diphosphonic acid (HEDP), phytic acid, diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), aminoethyl ethanolamine (AEEA), glutamic acid N,N-diacetic acid (GLDA), 1,3-propylenediamine tetraacetic acid (PDTA), glucoheptonic acid, dipicolinic acid, ethylene diamine tetra (methylene phosphonic acid) (EDTMPA), 2-hydroxyethyliminodiacetic acid (HEIDA) or water soluble salts thereof or mixtures thereof.

ANTI-REDEPOSITION AGENTS

[0073] The composition of the present invention may optionally comprise one or more anti-redeposition agents.

[0074] The main function of anti-redeposition agents is the aid to prevent the soil from redepositioning on the washing substrate when a washing liquor provides insufficient soil anti-redeposition capacity.

[0075] Anti-redeposition agent(s) can provide their effect by becoming adsorbed irreversibly or reversibly to the soil particles or to the substrate. Thereby the soil becomes better dispersed in the washing liquor or the substrate is occupied with anti-redeposition agent(s) on those places the soil could redeposit.

[0076] The anti-redeposition agent(s) that are known to be used in detergent compositions include, but are not limited to, carboxymethyl cellulose, polyester-PEG co-polymer, polyvinyl pyrrolidone based polymers etc.

BLEACHING AGENTS

[0077] The composition of the present invention may optionally comprise one or more bleaching agents.

[0078] Bleaching agents can be used in a detergent composition either alone or in combination with a bleach activator and/or a bleach catalyst. The function of the bleaching agent is the removal of bleachable stains and to achieve an antibacterial effect on the load and inside of the (dish)washing machine.

[0079] Bleaching agents commonly used as a sole bleaching ingredient in detergents react with the soil.

[0080] When an inorganic oxygen based bleaching agent is used in combination with a bleach activator it does react with the bleach activator. One of the reaction product provides the actual performance.

[0081] When an inorganic oxygen based bleaching agent is used in combination with a bleach catalyst the catalyst catalyses the oxidation reaction with the substrate. The oxidized bleach catalyst provides the actual bleach performance. A bleach activator can optionally be present.

[0082] Bleaching agents that can be used in detergent compositions include, but are not limited to, active chlorine compounds, inorganic peroxygen compounds and organic peracids. Examples are sodium percarbonate, sodium perborate monohydrate, sodium perborate tetrahydrate, hydrogen peroxide, hydrogen peroxide based compounds, persulfates, peroxymonosulphate, peroxodisulphate, ϵ -phthalimido-perox-caproic acid, benzoyl peroxide, sodium hypochlorite,

sodium dichloroisocyanurate, etc. as well as mixtures thereof.

BLEACH ACTIVATORS

5 [0083] The composition of the present invention may optionally comprise one or more bleach activators.

[0084] When inorganic peroxygen based bleaching agents are applied, a bleach activator provides the possibility to use a comparatively low temperature to achieve the desired bleaching performance. The bleach activator reacts with the peroxygen to form an organic peracid. Depending from the used bleach activator these peracids can have a hydrophobic or a hydrophilic character.

10 [0085] Bleaching agents that can be used in detergent compositions include, but are not limited to, tetraacetylene-diamine (TAED), sodium nonanoyloxybenzene sulfonate (NOBS), acetyl caprolactone, N-methyl morpholinium acetonitrile and salts thereof, sodium 4-(2-decanoxyethoxycarbonyloxy)benzenesulfonate (DECOBS) and salts thereof, etc.

15 BLEACH CATALYSTS

[0086] The composition of the present invention may optionally comprise one or more bleach catalysts.

[0087] A bleaching catalyst can be used besides to or instead of a bleach activator. Most activators used are complexes of transition metal ions with organic ligands. Metal ions that may be applied in catalysts are manganese, iron, copper, cobalt and molybdenum. Complexes including these metals can interact with inorganic and organic peroxygen compounds to form reactive intermediates. The use of a bleach catalyst can result in achieving the desired bleaching performance at an even lower temperature than needed for bleach activators.

20 [0088] Bleaching catalysts that can be used in detergent compositions are intensively described in the state of the art. These include, but are not limited to a complex of manganese(IV) with 1,4,7-trimethyl-1,4,7-triazacyclononane (MnMe₃TACN), tris[2-(salicylideneamino)ethyl]amine manganese(III), siderophore-metal complexes (as described e.g in WO 2008/101909, metal complexes containing ligands of 1,4,7-triazacyclononan (TACN), manganese-protein complexes, etc.

30 DYES

30 [0089] The composition of the present invention may optionally comprise one or more dyes. The dye is used to colour the detergent, parts of the detergent or speckles in the detergent. This might render the product more attractive to the consumer.

[0090] Dyes that can be used in detergent compositions include, but are not limited to, Nylosan yellow N-7GL, Sanolin brilliant flavine 8GZ, Sanolin yellow BG, Vitasyn quinoline yellow 70, Vitasyn tartrazine X90, Puricolor yellow AYE23, Basacid yellow 232, Vibracolor yellow AYE17, Simacid Eosine Y, Puricolor red ARE27, Puricolor red ARE14, Vibracolor red ARE18, Vibracolor red ARE52, Vibracolor red SRE3, Basacid red 316, Ponceau SX, Iragon blue DBL86, Sanolin blue EHRL, Sanolin turquoise blue FBL, Basacid blue 750, Iragon blue ABL80, Vitasyn blue AE90, Basacid blue755, Vitasyn patentblue V 8501, Vibracolor green AGR25. These dyes are available at the firms Clariant or BASF.

40 PERFUME

[0091] The composition of the present invention may optionally comprise one or more perfumes. The perfume is added to the detergent to improve the sensorial properties of the product or of the machine load after cleaning.

45 [0092] The perfume can be added to the detergent as a liquid, paste or as a co-granulate with a carrier material for the perfume. To improve the stability of the perfume it can be used in an encapsulated form or as a complex like for example a perfume-cyclodextrine complex.

[0093] Also perfumes that have a deodorizing effect can be applied. Such perfumes or raw materials encapsulate malodours by binding to their sulphur groups.

50 PROCESS AIDS

[0094] The composition of the present invention may optionally comprise one or more process aids. Process aids are used to improve certain product or production properties.

55 [0095] The process aids used in detergent compositions commonly are used for various purposes often depending of the physical form of the final product. Process aids for example can optimize compressibility, friability, toughness, elasticity, disintegration speed, hygroscopicity, density, free flowing properties, stickiness, viscosity, rheology, etc. of a detergent product in a certain physical shape. Such process aids are widely described in the state of the art.

[0096] In a particular preferred embodiment of the detergent composition of the present invention, said composition includes a compressed detergent part and a non-compressed rinse aid. The compressed detergent part may comprise about 1 to 10 wt.-% of one or more surfactants, preferably non-ionic surfactants, and/or about 1 to 10 wt.-% of one or more enzymes, and/or about 3 to 50 wt.-% of one or more silicates, including alkali metal disilicates and/or alkali metal aluminosilicates or a mixture thereof, and/or about 5 to 15 wt.-% of one or more bleaching agents, and/or about 2 to 15 wt.-% of one or more bleach activators, and/or about 1 to 20 wt.-% of one or more polymeric organic (co)builder and/or dispersing agents, and/or about 10 to 70 wt.-% of one or more organic chelating agents of low molecular weight ($M_w < 750$ g/mol, preferably $M_w < 500$ g/mol), acting as a (co)builder, dispersing agent, corrosion agent, complexing agent and/or redeposition agent, and/or about 10 to 70 wt.-% of one or more inorganic non-phosphate builder, also acting as an alkalinity source, all of the amounts based on the total weight of the composition including the compressed as well as the non-compressed part. Preferably, the compressed part may include a combination of all of these compounds in the amount given above. The non-compressed part preferably may comprise more than 50 wt.-% based on the weight of the non-compressed part, of a semi-solid surfactant as described above. The remaining part of the rinse aid additive preferably may be formed by one or more solids as described above, preferably selected from group comprising alkali metal silicates, including alkali metal aluminosilicates, gums, including xanthan and guar gum, organic waxes and fat, including modified organic oils solid at room temperature, metal oxides, including zinc oxides and inorganic builders and/or alkalinity sources, including sodium carbonate. The amount of rinse additive in the total detergent composition of the present invention preferably may be in the range of from 0.4 to 10 wt.-%, more preferably of from 0.6 to 8 wt.-% e.g. including 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, and 7.5 wt.-%, based on the total weight of the composition, including the compressed as well as the non-compressed part.

[0097] The present invention further includes the use of the rinse aid additive and/or the detergent composition of the present invention for cleaning and/or rinsing tableware, dishware, cookware and/or flatware, preferably in automatic dishwashing.

EXAMPLES

EXAMPLE 1

[0098] Example 1 shows the positive effect on rinse-aid performance of a blend of a semi-solid surfactant with a solid compound, wherein the mixture is provided as a solid non-compressed part on a compressed automatic dishwashing detergent composition.

[0099] All ingredients of the detergent compositions are expressed in parts.

Detergent composition	A	B
COMPRESSED PART OF EMBODIMENT		
Raw-materials		
Trisodium citrate	25	25
Sodium carbonate	16	16
Sodium disilicate	5	5
Tetrasodium iminodisuccinate	20	20
Glutamic acid-N,N-diacetic tetrasodium salt	6	6
Phosphonate	0.3	0.3
Coated sodium percarbonate	10	10
Tetraacetyl ethylenediamine	4.5	4.5
Sulfonated polymer ⁽¹⁾	5	5
Maleic acid/olefin co-polymer ⁽²⁾	1	1
Protease ⁽³⁾	2	2
Amylase ⁽⁴⁾	0.60	0.60
Fatty alcohol ethoxylate ⁽⁵⁾	4.4	4.4
Dipropionate ⁽⁶⁾	0.2	0.2
total compressed part	100	100
NON-COMPRESSED PART OF EMBODIMENT		
Raw-materials		
Semi-solid surfactant	2	2

(continued)

NON-COMPRESSED PART OF EMBODIMENT		
Sodium aluminosilicate (7)		1
total non-compressed part	2.0	3
TOTAL	102	103
(1) like Sokalan CP50 (BASF), Alcoguard 4100, 4085 or 4140, Alcosperse 240 (AkzoNobel), Acusol 587 or 588 (Rohm&Haas), (2) like Sokalan CP9, (3) like Excellase, Properase, Purafect, Purafast (Genencor), Ovozyme, Everlase, Savinase, Polarzyme (Novozymes), Kemzym (Kemira), (4) like Purastar, Duramyl, Powerase (Genencor), Ter-mamyl, Stainzyme, Stainzyme Plus (Novozyme), Kemzym (Kemira), (5) like Lutensol AT25, AT80, Emulan AT9 (BASF), (6) like AMA100 (Lakeland), (7) like Tioxolex 25 and 28 (Rhodia), Valfor 100 Zeolite Na A (PQ Corporation).		

[0100] The compressed parts of the compositions weight 17.5 grams. The non-compressed parts of the compositions were in the form of a straight stripe on the surface of the compressed parts. The semi-solid surfactant used in this test was Emulan AT9 (BASF).

Rinse-aid test

[0101] To determine the rinse performance of multifunctional automatic dishwashing detergent compositions they were tested in an automatic dishwashing machine, with a clean test load, a ballast soil mix and water of 21°GH.

[0102] The results are evaluated with reference to the number and intensity of spots and to the intensity and nature of the filming. For determination of the spots the 'normal 50' program of a Miele G698 dishwasher was used. For determination of the filming the 'eco 50' program of a Bosch SGS57 dishwasher was used. In all the dishwashing machines used in this test the water-softener unit was made inoperative.

[0103] During each run in a dishwasher ballast soil was dosed in the machine at the beginning of the main cycle. The main ingredients of this ballast soil, besides water, were fat, egg and starch.

[0104] The clean test load in the dishwasher contained four types of glasses, a cocktail glass and a whiskey glass (both from the Schott Zwiesel brand), an Altbier glass and a Willy beaker glass (both from RKL Ruhr Kristall Glas). The load also contained three types of plates, a dark blue Melamine plate (Rosti Mepal), a transparent dish (from Tupperware) and a black porcelain plate (from Friesland porcelain factory).

The load furthermore contained a butter box (from APS) and three types of knives (Kent from WMF, Cult from BSF, J.A. Henckels and Yes from Michelin).

[0105] Of each of these items three pieces were present in the dishwasher. Further the dishwasher contained several plates that were used as ballast load but were not evaluated in the test.

[0106] Before the tests started the load was washed with a strong alkaline dishwasher detergent composition followed by a rinse with acidic acid.

[0107] Each load in the machines was washed 6 times with the automatic dishwashing detergent composition which was tested. For determining the performance of the respective detergent composition the loads after cycles 4, 5 and 6 were evaluated with reference to spots, filming and side effects. The average score for these three washing cycles is reported.

[0108] The score on spots is the average of the score that was obtained in view of the intensity of the spots and the number of spots found on the test load. In the table below a description of the score is shown.

45
 10 = no spots
 9 = very low intensity/number of spots
 7 = low intensity/number of spots
 5 = medium intensity/number of spots
 3 = high intensity/number of spots
 1 = very high intensity/number of spots

[0109] The score on filming on the test load was evaluated on the intensity of the filming and the nature of the filming according to the table below. With a closed nature of the filming is meant that the film is homogeneous, open nature means that the filming is inhomogeneous.

55
 10 = no filming
 9 = very low intensity of the filming

8 = low intensity of the filming with a closed nature
 7 = low intensity of the filming with an open nature
 6 = medium intensity of the filming with a closed nature
 5 = medium intensity of the filming with an open nature
 5
 4 = high intensity of the filming with a closed nature
 3 = high intensity of the filming with an open nature
 2 = very high intensity of the filming with a closed nature
 1 = very high intensity of the filming with an open nature

10 [0110] Since the test on filming and spots is performed in two different machines the load was, besides filming or spots, also considered in regard to negative side effects like filming in a spotting test and spots in a filming test. These side effects are ranked according to the list below.

15 5 = no side effects
 4 = minor side effects
 3 = clearly visible side effects
 2 = very strong side effects
 1 = unacceptable side effects

20 [0111] Detergent compositions A and B have been tested in view of the above criteria and the results are listed below.

Score on the number and intensity of spots;

Composition	Glass	Plastics	Porcelain	Steel	Average
A	3.1	3.9	3.2	2.9	3.3
B	5.8	3.6	6.8	4.7	5.2

Score on side-effect during the spotting test;

Composition	Glass	Plastics	Porcelain	Steel	Average
A	1.6	3.7	2.8	3.0	2.8
B	2.1	4.4	3.9	3.8	3.6

Score on the intensity and nature of filming;

Composition	Glass	Plastics	Porcelain	Steel	Average
A	4.9	7.7	5.7	6.5	6.2
B	5.0	7.4	5.8	6.1	6.1

Score on side-effect during the filming test;

Composition	Glass	Plastics	Porcelain	Steel	Average
A	1.7	3.6	3.7	1.8	2.7
B	2.0	3.9	4.6	2.3	3.2

50 [0112] These results show that with respect to spotting composition B (comprising a rinse aid mixture of a surfactant and solid additive) has a better score than composition A (only comprising the surfactant without the solid additive). Also the side-effects found in this spotting test are less for composition B when compared to composition A.

[0113] The results of the filming test show that composition A and B have a comparable score on filming, the side-effects during filming, however, are lower for the inventive composition B.

[0114] The blend of the surfactant with a solid compound gives a better result particularly in view of spots on glass, porcelain and stainless steel as just the same semi-solid surfactant without the solid compound.

Drying test

[0115] To determine the drying performance of multifunctional automatic dishwashing detergent compositions they were tested in an automatic dishwashing machine, with a clean test load, a ballast soil mix and water of 21°GH.

5 [0116] The results are evaluated with reference to the number of remaining water drops on the dishwasher load. For determination of the drying effect the 'eco 50' program of a Bosch SGS57 dishwasher was used. In the dishwashing machines used in this test the water-softener unit was made inoperative.

10 [0117] During each run in a dishwasher ballast soil was dosed in the machine at the beginning of the main cycle. The main ingredients of this ballast soil, besides water, were fat, egg and starch.

15 [0118] The clean test load in the dishwasher contains glassware, plastics, stainless steel and porcelain; in particular 12 borosilicate glasses, 3 plastic plates (SAN), 3 plastic plates (PP), 3 plastic bowls (PP), 3 plastic boxes (PP), 8 porcelain soup plates, 11 porcelain dinner plates, 7 porcelain dessert plates, 10 porcelain cups, 12 knifes, 6 forks, 6 soup spoons, 6 dessert spoons, 6 tea spoons, 1 sauce spoon, 1 serving spoon and 1 serving fork.

20 [0119] Before the tests started the load was washed with a strong alkaline dishwasher detergent composition followed by a rinse with acidic acid.

[0120] Each load in the machines was washed 6 times with detergent composition A or B, respectively. For determining the performance of the respective detergent composition the loads after cycles 4, 5 and 6 were evaluated with reference to remaining water drops per item of the dishwasher load. The average score for these three washing cycles is reported.

25 [0121] After the drying step the doors were kept closed for 30 minutes. Then the drying performance was assessed by determining the remaining water drops on the dishwasher load as quick as possible according to table below.

Score	Number of drops
0	None
1	1
2	2
3	3
4	4
5	5
6	>5

30 [0122] Detergent compositions A and B have been tested in view of the above criteria and the results are listed below.

35 Score on the drying performance;

Composition	Glass	Plastics	Porcelain	Steel	Average
A	0.4	2.9	0.7	0.5	1.1
B	0.2	1.8	0.5	0.4	0.7

40 [0123] The score given for each type of material (glass, plastics, porcelain, steel) is the average score of all items made of this material.

45 [0124] These results show that with respect to the drying performance composition B (comprising a rinse aid mixture of a surfactant and a solid additive) has a better score than composition A (only comprising the surfactant without the solid additive).

EXAMPLE 2

50 [0125] Example 2 shows the effects of several different solid compounds in the blend.

Example detergent compositions C to H;

[0126] All ingredients of the detergent compositions are expressed in parts.

COMPRESSED EMBODIMENT	C	D	E	F	G	H
Raw-materials						

(continued)

	C	D	E	F	G	H
COMPRESSED EMBODIMENT						
5	Trisodium citrate	23.3	23.3	23.3	23.3	23.3
	Sodium carbonate	15	15	15	15	15
	Sodium disilicate	5	5	5	5	5
	Tetrasodium iminodisuccinate	19	19	19	19	19
10	Glutamic acid-N,N-diacetic acid tetra sodium salt	5	5	5	5	5
	Phoshonate	0.3	0.3	0.3	0.3	0.3
	Coated sodium percarbonate	11	11	11	11	11
	Tetraacetyl ethylenediamine	4.2	4.2	4.2	4.2	4.2
15	Sulfonated polymer (1)	4.8	4.8	4.8	4.8	4.8
	Maleic acid/olefin co-polymer (2)	0.8	0.8	0.8	0.8	0.8
	Protease (3)	1.7	1.7	1.7	1.7	1.7
	Amylase (4)	0.7	0.7	0.7	0.7	0.7
	Fatty alcohol ethoxylate (5)	4.2	4.2	4.2	4.2	4.2
20	Dipropionate (6)	0.2	0.2	0.2	0.2	0.2
	Sodium	2	2	2	2	2
	total compressed part	97.2	97.2	97.2	97.2	97.2
NON-COMPRESSED PART OF EMBODIMENT						
25	Raw-materials					
	Semi-solid surfactant	1.9	1.9	1.9	1.9	1.9
	Sodium aluminosilicate (7)	0.9				
	Guar-gum (8)		0.9			
	Organic derivate of castor oil (9)			0.9		
30	Zinc oxide (10)				0.9	
	Sodium carbonate (11)					0.9
	total non-compressed part	2.8	2.8	2.8	2.8	2.8
	TOTAL	100	100	100	100	100
35	(1) like Sokalan CP50 (BASF), Alcoguard 4100, 4085 or 4140, Alcosperse 240 (AkzoNobel), Acusol 587 or 588 (Rohm&Haas), (2) like Sokalan CP9, (3) like Excellase, Properase, Purafect, Purafast (Genencor), Ovozyme, Everlase, Savinase, Polarzyme (Novozymes), Kemzym (Kemira), (4) like Purastar, Duramyl, Powerase (Genencor), Termamyl, Stainzyme, Stainzyme Plus (Novozyme), Kemzym (Kemira), (5) like Lutensol AT25, AT80, Emulan AT9 (BASF), (6) like AMA100 (Lakeland), (7) like Tixolex 25 and 28 (Rhodia), Valfor 100 Zeolite Na A (PQ Corporation), (8) like Jaguar HP120 (Harke Chemicals), (9) like Thixin-R (Elementis Specialties), (10) like Zinc white (Quaron), (11) sodium carbonate with an average particle size below 0.3 millimeter (Solvay).					
40						

[0127] The weight of 100 parts of detergent compositions C to H was 18.0 grams. The non-compressed part of composition C to H had a round shape with a diameter between 16 and 30 millimetres. The semi-solid surfactant used in this test was Emulan AT9 (by BASF).

Rinse-aid test

[0128] To determine the rinse performance of multifunctional automatic dishwashing detergent compositions they were tested in an automatic dishwashing machine, with a clean test load, a ballast soil mix and water of 21 °GH.

[0129] The results are evaluated with reference to the number and intensity of spots and to the intensity and nature of the filming. For this test a Miele GSL (G1222SC) with program 4, R-Zeit 2 was used (cleaning at 50 °C and rinsing at 65 °C). In all the dishwashing machines used in this test the water-softener unit was made inoperative.

[0130] During each run in a dishwasher ballast soil was dosed in the machine at the beginning of the main cycle. The main ingredients of this ballast soil, besides water, were fat, egg and starch.

[0131] The clean test load in the dishwasher contained four glasses, three plates, a plastic box and a knife, all of which are described in more detail below;

- Pasis beerglass, 275 ml, form 4858-42, Schott Zwiesel by Zwiesel Kristallglass AG.
- Mondial waterglass, 323 ml, form 7500, Schott Zwiesel by Zwiesel Kristallglass AG.
- Cola glass, professioneel stapelbaar klein, 22 cl, article number 610.02153, Select dinnerware by Hanos.
- Whiskey glass Islande, 20 cl, Arcoroc by Arc International.

5

- Melamine plate by Rosti Mepal.
- Black porcelain plate, Teller flach Fahne 1030/20 by Bauscher.
- SAN plate, blue, WACA by WACA-Kunststoffwarenfabrik, Heinrich Walch GmbH + Co. KG.
- Plastic box, blue, 600 ml, low model, Tupperware by Tupperware Brands Corporation.
- 10 Stainless steel monoblock knife, Vorspeise- /Dessertmes, type Berlin, WMF by WMF Württembergische Metallwarenfabrik AG.

[0132] Of each of these items one piece was present in the dishwasher, further the dishwasher contained a ballast load that will not be assessed.

15 [0133] Before the tests started the load was washed with a strong alkaline dishwasher detergent followed by a wash with citric acid.

[0134] Each machine washed the load six times with the respective automatic dishwashing detergent composition that was tested. For determination of the performance of the detergent composition the load of cycles 4, 5 and 6 were evaluated with reference to spots and filming. The final score on spots and on filming is an average of these three evaluations.

20 [0135] The score on spots is the average of the score that was obtained in view of the intensity of the spots and the number of spots found on the test load. In the table below a description of the score is shown.

10 = no spots

9 = very low intensity/number of spots

25 7 = low intensity/number of spots

5 = medium intensity/number of spots

3 = high intensity/number of spots

1 = very high intensity/number of spots

30 [0136] The score on filming on the test load was evaluated on the intensity of the filming and the nature of the filming according to the table below.

10 = no filming

35 9 = very low intensity of the filming

8 = low intensity of the filming with a closed nature

7 = low intensity of the filming with an open nature

6 = medium intensity of the filming with a closed nature

5 = medium intensity of the filming with an open nature

40 4 = high intensity of the filming with a closed nature

3 = high intensity of the filming with an open nature

2 = very high intensity of the filming with a closed nature

1 = very high intensity of the filming with an open nature

45 [0137] Detergent compositions C to H have been tested according to the above described method. The results are listed below.

Score on the number and intensity of spots;

Composition	Glass	Plastic	Porcelain	Steel	Average
C	6.8	5.3	6.9	5.0	6.0
D	6.5	5.4	5.7	4.0	5.4
E	6.8	5.1	6.3	4.0	5.5
F	6.5	5.3	5.7	4.0	5.4
G	6.9	5.5	6.0	5.0	5.9
H	6.0	5.4	6.0	5.0	5.6

Score on the intensity and nature of filming;

Composition	Glass	Plastic	Porcelain	Steel	Average
C	4.7	6.0	4.3	4.0	4.8
D	5.2	5.5	4.5	5.0	5.1
E	4.7	6.0	3.3	5.0	4.8
F	4.7	6.0	4.0	5.0	4.9
G	5.0	6.3	3.5	4.0	4.7
H	3.6	4.8	2.0	2.7	3.3

[0138] These results show that even though the compositions have a comparable score on spotting, but that the results in the test are poor when no solid compound is present in the rinse aid (composition H).

Claims

1. A rinse aid additive for automatic dishwashing provided in form of a

- (i) non-compressed part attached to a compressed detergent composition, or
- (ii) non-compressed part separate of a compressed or non-compressed detergent composition in any shape that can be dosed separate from a detergent, or
- (iii) granulate that is contained in a compressed or non-compressed detergent composition.

comprising more than 40 wt.-% based on the total weight of the rinse aid additive of surfactant, possessing a dynamic viscosity of equal or greater than 10^5 mPa·s at a temperature of 20 °C, which drops in the temperature interval of between above 20 °C to about 40 °C by a factor of 25 per 10°C or more, and at least one solid compound, wherein said rinse aid additive is in form of a solid at room temperature.

2. Rinse aid additive according to claim 1, wherein the surfactant is selected from the group consisting of fatty alcohol derivatives, preferably ethoxylated fatty alcohols, mixtures of fatty alcohol ethoxylates, fatty acid ethoxylates, ethoxylated Gemini-surfactants, or mixtures thereof.

3. Rinse aid additive according to claims 1 or 2, wherein the solid compound is a particulate solid compound.

4. Rinse aid additive according to claim 3, wherein the solid compound has a particle size distribution from 0.1 µm to 2 mm.

5. Rinse aid additive according to any of claims 1 to 4, wherein the solid compound is selected from the group consisting of water soluble salts, water insoluble salts, silicates, silicate comprising compositions, waxes and homo-, co- or ter-polymers of olefins, acrylic, methacrylic or maleic acids, optionally further functionalized by sulfonated groups, or salts thereof, polyethylene glycols having a molecular weight of above 7000, polysaccharides, in particular gums, alginate, carboxymethyl cellulose, starches, collagen, gelatine, tapioca, citrate or tripolyphosphate in the form of a potassium or sodium salt, citric acid, tetraacetylenediamine, triazole-compounds, or mixtures thereof.

6. Rinse aid additive according to claim 5, wherein the solid compound is selected from the group consisting of sodium carbonate, sodium chloride, zinc oxide, sodium aluminum silicates, rheological additives based on organic derivates of vegetable oil, polysaccharides and fumed silicas

7. Method for preparing a rinse aid additive according to any of claims 1 to 6, wherein the solid compound is combined at least with a surfactant, possessing a dynamic viscosity of equal or greater than 10^5 mPa·s at a temperature of 20 °C, which drops in the temperature interval of between above 20 °C to about 40 °C by a factor of 25 per 10°C or more, optionally the mixture is heated to a temperature above the temperature where the surfactant becomes waxy or at least partially liquid, blending the solid at least with the surfactant and allowing the blend to cool to a temperature where the blend becomes solid.

8. A detergent composition comprising a rinse aid additive according to any of claims 1 to 6.
9. Detergent composition according to claim 8, wherein the rinse aid additive is provided in form of a
 - 5 (i) non-compressed part attached to a compressed detergent composition, or
 - (ii) non-compressed part separate of a compressed or non-compressed detergent composition in any shape that can be dosed separate from a detergent, or
 - (iii) granulate that is contained in a compressed or non-compressed detergent composition.
10. Detergent composition according to claim 9, wherein the non-compressed part of the rinse aid additive according to (i) is provided as pearls, droplets, pellets, at least one ball, stripe(s), dot(s), strand(s), extruded line(s), or a pattern in or on the compressed portion of the detergent composition or as a coating on or around at least a part of the surface of the compressed portion or non-compressed part of the rinse aid additive according to (ii) is provided as a powder, pearls, droplets, granulate, spheres, pellets, tablet(s), ball(s) or cube(s).
- 15 11. Use of a blend solid at room temperature, comprising more than 40 wt.-%, based on the total weight of the rinse aid additive, of a surfactant, possessing a dynamic viscosity of equal or greater than 10^5 mPa·s at a temperature of 20 °C, which drops in the temperature interval of between above 20 °C to about 40 °C by a factor of 25 per 10°C or more, and at least one solid compound as a rinse aid additive provided in form of a
 - 20 (i) non-compressed part attached to a compressed detergent composition, or
 - (ii) non-compressed part separate of a compressed or non-compressed detergent composition in any shape that can be dosed separate from a detergent, or
 - (iii) granulate that is contained in a compressed or non-compressed detergent composition,
- 25 in combination with an automatic dishwasher detergent composition to increase rinse performance of the detergent composition.
- 30 12. Use of a rinse aid additive according to any of claims 1 to 6 or a detergent composition according to any of claims 8 to 10 for cleaning and/or rinsing tableware, dishware, cookware and/or flatware, preferably in automated dish-washing.

Patentansprüche

- 35 1. Ein Klarspülzusatz für das Maschinengeschirrreinigen, das in Form eines
 - (i) nicht verpressten Teils, der an eine verpresste Reinigungsmittelzusammensetzung angelagert ist, oder
 - (ii) nicht verpressten Teils, getrennt von einer verpressten oder nicht verpressten Reinigungsmittelzusammensetzung in jeglicher Form, die getrennt von einem Reinigungsmittel dosiert werden kann, oder
 - 40 (iii) Granulats, das in einer verpressten oder nicht verpressten Reinigungsmittelzusammensetzung enthalten ist, bereitgestellt wird, enthaltend mehr als 40 Gew.-%, bezogen auf das Gesamtgewicht des Klarspülzusatzes, eines Tensids, das eine dynamische Viskosität von gleich oder größer 10^5 mPa·s bei einer Temperatur von 20°C aufweist, die in dem Temperaturintervall von zwischen oberhalb 20°C bis ungefähr 40°C um einen Faktor von 25 pro 10°C oder mehr abfällt, und wenigstens eine feste Verbindung, wobei der Klarspülzusatz bei Raumtemperatur in Form eines Feststoffs vorliegt.
2. Klarspülzusatz gemäß Anspruch 1, wobei das Tensid ausgewählt ist aus der Gruppe, bestehend aus Fettalkohol-derivaten, bevorzugt ethoxylierten Fettalkoholen, Mischungen von Fettalkoholethoxylaten, Fettsäureethoxylaten, ethoxylierten Gemini-Tensiden oder Mischungen daraus.
3. Klarspülzusatz gemäß Anspruch 1 oder 2, wobei die feste Verbindung eine teilchenförmige feste Verbindung darstellt.
- 55 4. Klarspülzusatz gemäß Anspruch 3, wobei die feste Verbindung eine Partikelgrößenverteilung von 0,1 µm bis 2 mm aufweist.
5. Klarspülzusatz gemäß einem der Ansprüche 1 bis 4, wobei die feste Verbindung ausgewählt ist aus der Gruppe,

bestehend aus wasserlöslichen Salzen, wasserunlöslichen Salzen, Silicaten, silicathaltigen Zusammensetzungen, Wachsen und Homo-, Co- oder Terpolymeren von Olefinen, Acrylsäure, Methacrylsäure oder Maleinsäure, gegebenenfalls weiter funktionalisiert durch sulfonierte Gruppen, oder Salze davon, Polyethylenglykolen mit einem Molekulargewicht von oberhalb 7.000, Polysacchariden, insbesondere Gummiharze, Alginat, Carboxymethylcellulose, Stärken, Collagen, Gelatine, Tapioka, Citrat oder Tripolyphosphat in Form eines Kalium- oder Natriumsalzes, Zitronensäure, Tetraacetylethylendiamin, Triazolverbindungen oder Mischungen daraus.

- 5 6. Klarspülzusatz gemäß Anspruch 5, wobei die feste Verbindung ausgewählt ist aus der Gruppe, bestehend aus Natriumcarbonat, Natriumchlorid, Zinkoxid, Natriumaluminiumsilicaten, rheologischen Additiven, die auf organischen Derivaten pflanzlicher Öle basieren, Polysacchariden und pyrogenen Kieselsäuren.
- 10 7. Verfahren zum Herstellen eines Klarspülzusatzes gemäß einem der Ansprüche 1 bis 6, wobei die feste Komponente wenigstens mit einem Tensid, das eine dynamische Viskosität von gleich oder größer $10^5 \text{ mPa}\cdot\text{s}$ bei einer Temperatur von 20°C , die in dem Temperaturintervall von zwischen oberhalb 20°C bis ungefähr 40°C um einen Faktor von 25 pro 10°C oder mehr abfällt, besitzt, kombiniert wird, die Mischung gegebenenfalls auf eine Temperatur oberhalb der Temperatur, bei der das Tensid wachsförmig oder wenigstens teilweise flüssig wird, erwärmt wird, der Feststoff wenigstens mit dem Tensid vermischt wird und das Gemisch auf eine Temperatur abkühlen gelassen wird, bei der das Gemisch fest wird.
- 15 8. Eine Reinigungsmittelzusammensetzung, enthaltend einen Klarspülzusatz gemäß einem der Ansprüche 1 bis 6.
- 20 9. Reinigungsmittelzusammensetzung gemäß Anspruch 8, wobei der Klarspülzusatz in Form eines
 - 25 (i) nicht verpressten Teils, der an eine verpresste Reinigungsmittelzusammensetzung angelagert ist, oder
 - (ii) nicht verpressten Teils, getrennt von einer verpressten oder nicht verpressten Reinigungsmittelzusammensetzung in jeglicher Form, die getrennt von einem Reinigungsmittel dosiert werden kann, oder
 - (iii) Granulats, das in einer verpressten oder nicht verpressten Reinigungsmittelzusammensetzung enthalten ist,
 - 30 bereitgestellt wird.
- 35 10. Reinigungsmittelzusammensetzung gemäß Anspruch 9, wobei der nicht verpresste Teil des Reinigungsmittelzusatzes gemäß (i) als Perlchen, Tropfen, Pellets, wenigstens ein Ball, Streifen, Punkt(e), Strang/Stränge, extrudierte Line(n) oder als ein Muster in oder auf dem verpressten Teil der Reinigungsmittelzusammensetzung oder als eine Beschichtung auf oder um wenigstens einen Teil der Oberfläche des verpressten Teils vorliegt oder der nicht verpresste Teil des Klarspülzusatzes gemäß (ii) als ein Pulver, Perlchen, Tropfen, Granulat, Kugeln, Pellets, Tablette(n), ballförmig oder kubusförmig bereitgestellt wird.
- 40 11. Verwendung eines bei Raumtemperatur festen Gemisches, enthaltend mehr als 40 Gew.-%, bezogen auf das Gesamtgewicht des Klarspülzusatzes, eines Tensids, das eine dynamische Viskosität von gleich oder größer als $10^5 \text{ mPa}\cdot\text{s}$ bei einer Temperatur von 20°C , die in dem Temperaturintervall von zwischen oberhalb 20°C bis ungefähr 40°C um einen Faktor 25 pro 10°C oder mehr abfällt, aufweist, und wenigstens eine feste Verbindung als ein Klarspülzusatz, bereitgestellt in Form eines
 - 45 (i) nicht verpressten Teils, der an eine verpresste Reinigungsmittelzusammensetzung angelagert ist, oder
 - (ii) nicht verpressten Teils, getrennt von einer verpressten oder nicht verpressten Reinigungsmittelzusammensetzung in jeglicher Form, die getrennt von einem Reinigungsmittel dosiert werden kann, oder
 - (iii) Granulats, das in einer verpressten oder nicht verpressten Reinigungsmittelzusammensetzung enthalten ist,
 - 50 in Kombination mit einer Maschinengeschirrreinigerzusammensetzung, um die Klarspülleistung der Reinigungsmittelzusammensetzung zu erhöhen.
- 55 12. Verwendung eines Klarspülzusatzes gemäß einem der Ansprüche 1 bis 6 oder einer Reinigungsmittelzusammensetzung gemäß einem der Ansprüche 8 bis 10 zum Reinigen und/oder Klarspülen von Tafelgeschirr, Kunststoff- oder Porzellangeschirr, Kochgeschirr und/oder Besteck, bevorzugt beim Maschinengeschirrreinigen.

Revendications

1. Adjuvant auxiliaire de rinçage pour lave-vaisselle automatiques, fourni sous forme
 - i) d'une partie non-comprimée, attachée à une composition de détergent comprimée,
 - ii) ou d'une partie non-comprimée, séparée d'une composition de détergent comprimée ou non-comprimée, sous toute forme qui puisse être dosée séparément d'un détergent,
 - iii) ou de granulés qui sont contenus dans une composition de détergent comprimée ou non-comprimée,
- 5 et comprenant plus de 40 %, en poids rapporté au poids total de l'adjuvant auxiliaire de rinçage, d'un tensioactif présentant une viscosité dynamique égale ou supérieure à 10^5 mPa.s à la température de 20 °C, laquelle chute d'un facteur de 25 ou plus par 10 °C dans l'intervalle de température allant de plus de 20 °C à environ 40 °C, et au moins un composant solide, et lequel adjuvant auxiliaire de rinçage se présente, à température ambiante, sous la forme d'un solide.
- 10
2. Adjuvant auxiliaire de rinçage, conforme à la revendication 1, dans lequel le tensioactif est choisi dans l'ensemble constitué par les dérivés d'alcools gras, de préférence les alcools gras éthoxylés, les mélanges de produits d'éthoxylation d'alcools gras, les produits d'éthoxylation d'acides gras, les tensioactifs « Gemini » éthoxylés, et les mélanges de ces composés.
- 15
3. Adjuvant auxiliaire de rinçage, conforme à la revendication 1 ou 2, dans lequel le composant solide est un composant solide en particules.
- 20
4. Adjuvant auxiliaire de rinçage, conforme à la revendication 3, dans lequel la distribution des tailles des particules du composant solide va de 0,1 µm à 2 mm.
- 25
5. Adjuvant auxiliaire de rinçage, conforme à l'une des revendications 1 à 4, dans lequel le composant solide est choisi dans l'ensemble formé par les suivants : sels solubles dans l'eau, sels insolubles dans l'eau, silicates, compositions comprenant un silicate, cires, homo-polymères, copolymères et terpolymères d'oléfines et d'acide acrylique, méthacrylique ou maléique, en option porteurs d'autres groupes fonctionnels qui sont des groupes sulfonates, ou de leurs sels, polyéthylèneglycols dont la masse molaire vaut plus de 7000, polysaccharides, en particulier gommes, alginates, carboxyméthyl-cellulose, amidons, collagène, gélatine, tapioca, citrate ou tripolyphosphate sous forme de sel de potassium ou de sodium, acide citrique, tétraacétyl-éthylène-diamine, et composés de type triazole, ainsi que leurs mélanges.
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- 35
6. Adjuvant auxiliaire de rinçage, conforme à la revendication 5, dans lequel le composant solide est choisi dans l'ensemble formé par les suivants : carbonate de sodium, chlorure de sodium, oxyde de zinc, silicates de sodium et d'aluminium, adjuvants rhéologiques à base de dérivés organiques d'huile végétale, polysaccharides, et silices de pyrohydrolyse.
- 40
7. Procédé de préparation d'un adjuvant auxiliaire de rinçage conforme à l'une des revendications 1 à 6, dans lequel le composant solide est combiné au moins avec un tensioactif présentant une viscosité dynamique égale ou supérieure à 10^5 mPa.s à la température de 20 °C, laquelle chute d'un facteur de 25 ou plus par 10 °C dans l'intervalle de température allant de plus de 20 °C à environ 40 °C, et le mélange est, en option, chauffé à une température supérieure à celle à laquelle le tensioactif devient cireux ou au moins en partie liquide, puis on mélange le solide au moins avec le tensioactif et on laisse le mélange refroidir jusqu'à une température où le mélange se solidifie.
- 45
8. Composition de détergent comprenant un adjuvant auxiliaire de rinçage conforme à l'une des revendications 1 à 6.
- 50
9. Composition de détergent conforme à la revendication 8, dans laquelle l'adjuvant auxiliaire de rinçage est fourni sous forme
 - i) d'une partie non-comprimée, attachée à une composition de détergent comprimée,
 - ii) ou d'une partie non-comprimée, séparée d'une composition de détergent comprimée ou non-comprimée, sous toute forme qui puisse être dosée séparément d'un détergent,
 - iii) ou de granulés qui sont contenus dans une composition de détergent comprimée ou non-comprimée.
- 55
10. Composition de détergent conforme à la revendication 9, dans laquelle la partie non-comprimée, dans l'adjuvant

auxiliaire de rinçage sous la forme (i), se présente sous forme de perles, de gouttelettes, de pastilles, d'au moins une bille, de bande(s), de point(s), de filet(s), de ligne(s) d'extrusion ou d'un motif intégré(s) dans ou sur la partie comprimée de la composition de détergent, ou bien sous forme d'un revêtement disposé sur au moins, ou autour d'au moins, une partie de la surface de cette partie comprimée, ou la partie non-comprimée, dans l'adjuvant auxiliaire de rinçage sous la forme (ii), se présente sous forme d'une poudre, de perles, de gouttelettes, de granulés, de sphères, de pastilles, de tablette(s), de bille(s) ou de cube(s).

5 **11.** Utilisation d'un mélange, solide à température ambiante, comprenant plus de 40 %, en poids rapporté au poids total de l'adjuvant auxiliaire de rinçage, d'un tensioactif présentant une viscosité dynamique égale ou supérieure à 10^5 10 mPa.s à la température de 20 °C, laquelle chute d'un facteur de 25 ou plus par 10 °C dans l'intervalle de température allant de plus de 20 °C à environ 40 °C, et au moins un composant solide, en tant qu'adjuvant auxiliaire de rinçage, fourni sous forme

15 i) d'une partie non-comprimée, attachée à une composition de détergent comprimée,
ii) ou d'une partie non-comprimée, séparée d'une composition de détergent comprimée ou non-comprimée,
sous toute forme qui puisse être dosée séparément d'un détergent,
iii) ou de granulés qui sont contenus dans une composition de détergent comprimée ou non-comprimée,

20 en combinaison avec une composition de détergent pour lave-vaisselle automatiques, pour améliorer la performance de rinçage de la composition de détergent.

25 **12.** Utilisation d'un adjuvant auxiliaire de rinçage conforme à l'une des revendications 1 à 6, ou d'une composition de détergent conforme à l'une des revendications 8 à 10, pour nettoyer et/ou rincer de la vaisselle de table, des plats et assiettes des couverts et/ou de la vaisselle de cuisine, de préférence dans un lave-vaisselle automatique.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 1524313 A [0005] [0051]
- EP 2071018 A [0006]
- WO 2005095570 A [0065]
- DE 19934704 A1 [0067]
- EP 1363986 A [0069]
- EP 1268729 A [0069]
- EP 299513 A1 [0069]
- EP 0877002 A [0069]
- WO 2008101909 A [0088]