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(54) **RINSE AID COMPOSITION CONTAINING WATER-SOLUBLE METAL SALT FOR USE IN AUTOMATIC DISHWASHING FOR METAL CORROSION AND RUST FORMATION PROTECTION**

SPÜLHILFSMITTEL ENTHALTEND WASSERLÖSLICHES METALLSALZ FÜR DEN GEBRAUCH IN EINER GESCHIRRSPÜLMASCHINE ZUM SCHUTZ VOR METALLKORROSION UND VERHINDERUNG DER ROSTBILDUNG

COMPOSITION D'AIDE AU RIN AGE CONTENANT UN SEL METALLIQUE HYDROSOLUBLE DESTINEE A ETRE UTILISEE DANS UN LAVE-VAISSELLE AUTOMATIQUE POUR LA PROTECTION CONTRE LA CORROSION DU METAL ET CONTRE LA FORMATION DE ROUILLE

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EP 1 578 895 B2

Description

FIELD OF THE INVENTION

[0001] The present invention is in the field of dishwashing, in particular it relates to automatic dishwashing products, auxiliaries and methods suitable for rinsing and protecting metal.

BACKGROUND OF THE INVENTION

[0002] Metal corrosion and rust formation in automatic dishwashing is a problem that continues to plague consumers, who now demand rinse aid products that will provide better metal care results. Use of water-soluble metal salts in automatic dishwashing to prevent glass corrosion is well known, however, use of water-soluble metal salts to prevent metal corrosion and rust formation in automatic dishwashing is new.

[0003] WO 95/21238 describes a cleaning composition for hand surfaces comprising an anticorrosion system consisting of a complex of at least one organic acid, of phosphoric acid and of N-alkyl-2-pyrrolidone, and having a pH in the range of 1 to 5.

[0004] One of the biggest problems with use of water-soluble metal salts in automatic dishwashing is that it can result in precipitation of insoluble materials on all types of hard surfaces. Such insoluble material is very undesirable to consumers as it can adhere to hard metal surfaces, such as stainless steel automatic dishwasher appliance parts, stainless steel flatware, stainless steel cookware, and stainless steel dishware, as well as on other hard surfaces such as, glassware, ceramics and plastics. The unwanted precipitation may be avoided by carefully adjusting the levels and proportions of various components in product formulation but this is costly and time consuming.

[0005] It has been surprisingly discovered that an acidic rinse aid composition containing both a water-soluble metal salt and a nonionic surfactant can effectively prevent metal corrosion and rust formation on hard metal surfaces, such as stainless steel, in automatic dishwashing appliances during operation. It has also been surprisingly found that by adding an acid, organic or inorganic acid, the insoluble precipitation on all hard surfaces can be avoided. Therefore, the rinse aid composition provides hard metal surface care (e.g. metal corrosion and rust formation prevention) without the negative of forming insoluble precipitates on flatware, dishes, glassware, cookware, or on the automatic dishwashing appliance parts themselves.

SUMMARY OF THE INVENTION

[0006] Disclosed herein is a rinse aid composition for reducing metal corrosion and rust formation characterized by comprising:

a) from about 0.01% to about 70% by weight of at least one water-soluble metal salt;
b) from about 0.01% to about 25% by weight of an acid;
c) from about 0.01% to about 60% by weight of a non-ionic surfactant;
d) a dispersant polymer, and
e) optionally at least one component selected from the group consisting of acid, dispersant polymer, perfume, hydrotrope, binder, carrier medium, antibacterial active, dye, and mixtures thereof;

wherein said rinse aid composition has a pH of less than about 5 when measured at a 10% concentration in an aqueous solution and wherein said at least one water-soluble metal salt comprises zinc and wherein said water-soluble zinc salt is selected from the group consisting of zinc acetate, zinc chloride, zinc gluconate, zinc formate, zinc malate, zinc nitrate, zinc sulfate, and mixtures thereof and wherein said dispersant polymer is a low molecular weight modified polyacrylate copolymer, wherein said copolymer contains as monomer units:

a) from about 90% to about 10% by weight acrylic acid or its salts, and
b) from about 10% to about 90% by weight of a substituted acrylic monomer or its salt and have the general formula:

$$-[(C(R^2)C(R^1)(C(O)OR^3)]-$$

wherein the incomplete valencies inside the square braces are hydrogen and at least one of the substituents R^1, R^2 or R^3 is a 1 to 4 carbon alkyl or hydroxyalkyl group, and wherein R^1 or R^2 can be a hydrogen and R^3 can be a hydrogen or alkali metal salt.

[0007] The acid enables the water-soluble metal salt to dissolve quickly in rinse liquor to at least partially reduce

formation of insoluble precipitates on hard surfaces.

DETAILED DESCRIPTION OF THE INVENTION

[0008] Metal corrosion and rust formation on metal components, flatware and dishware, including but not limited to, the stainless steel components of an automatic dishwashing appliance, can be prevented by delivering a water-soluble metal salt in the form of a rinse aid composition during automatic dishwashing operation. Use of a rinse aid composition containing a water-soluble metal salt and a nonionic surfactant can effectively prevent metal corrosion and rust formation during the automatic dishwashing operation.

[0009] A rinse aid composition is disclosed herein which contains from about 0.01 % to about 70% by weight of at least one water-soluble metal salt for use in an automatic dishwashing appliance to improve metal corrosion and rust formation protection without resulting in excessive precipi- tation in the wash and/or rinse liquor or on hard surfaces at the completion of the wash and/or rinse cycle. Formulating the water-soluble metal salt with an acid, either organic or inorganic, can at least partially reduce precipitation. About 0.01% to about 25% by weight of an acid is added to the rinse aid composition to enable the water-soluble metal salt to fully dissolve in the rinse aid composition and thereby reducing the chances of precipitate formation on hard surfaces, such as dishware, flatware, and glassware, during the wash and/rinse cycle. The addition of a perfume to the composition improves the odor profile of the consumer rinse aid product before, as well as, during the operation of the automatic dishwasher.

[0010] To provide metal corrosion and rust formation protection of stainless steel items, such as flatware, dishware, and metal components inside an automatic dishwashing appliance, water-soluble salts of zinc are used in the rinse aid composition, specifically zinc acetate, zinc chloride, zinc gluconate, zinc formate, zinc malate, zinc nitrate, zinc sulfate.

[0011] The rinse aid composition may be in any suitable form, including liquid, gel, solid, granular, powder, and combinations thereof. The solid water-soluble metal salt may be in the form of a powder, crystal, core particle, aggregate of core particles, prill, agglomerate, and mixtures thereof. These solid forms may be nonfriable for handling purposes during processing and when used by consumers.

[0012] In one non-limiting embodiment, further water-soluble salts of at least one metal selected from the group consisting of aluminium, magnesium, calcium, lanthanum, tin, gallium, strontium, titanium, and mixtures thereof, may be used in the rinse aid composition.

[0013] The water-soluble metal salt can be used directly as the raw material in the rinse aid composition or it can be provided as an additive compound or product which may be added along with other components to form the rinse aid composition.

[0014] The rinse aid composition may, for example, deliver any suitable amount of the water-soluble metal salt compound and/or product in the rinse liquor. For example, the rinse aid composition may, for example, deliver from 0.01 mM to 10 mM, alternatively 0.02 mM to 5 mM, alternatively 0.05 mM to 1 mM, and alternatively 0.05 mM to 0.5 mM of the water-soluble metal salt.

[0015] The rinse aid composition may be designed to deliver any suitable amount of metal ions in any suitable form in the rinse liquor of an automatic dishwashing appliance. For example, the rinse aid composition may be designed to deliver from 0.1% to 20%, alternatively from 0.2% to 15%, alternatively from 0.5% to 10%, and alternatively from 1% to 5% by weight of metal ions in the form of a water soluble metal salt rinse aid composition and/or product in the rinse liquor of an automatic dishwashing appliance.

[0016] The water-soluble metal salt is present in an amount from 0.01% to 70%, alternatively from 0.1% to 50%, alternatively from 0.5% to 30%, and alternatively from 1% to 10% by weight of the composition.

Zinc Salt

[0017] The present invention includes a water-soluble zinc salt selected from the group consisting of zinc acetate, zinc chloride, zinc formate, zinc gluconate, zinc malate, zinc nitrate, zinc sulfate, and mixtures thereof.

[0018] Water-soluble zinc salt can also be formed in-situ by reacting zinc oxide and an acid in rinse aid formulations. Any acid, organic or inorganic, that does not result in precipitation of the zinc salt in the composition after mixing can also be used. In one embodiment, a rinse aid composition may comprise a water-soluble zinc salt, which is prepared in-situ by mixing zinc oxide with an acid, For example, in the formulation of a liquid rinse aid composition, the components are mixed until all powder is dissolved to give a clear solution. After the in-situ neutralization process, other, ingredients can be added into the liquid mixture to formulate a liquid rinse aid composition. In another example, a binder or a solid surfactant (e.g. solid at 25°C) may be used to formulate the solid rinse aid composition.

[0019] In one non-limiting embodiment, the rinse aid composition may be designed to deliver from 0.1% to 20% by weight of Zn^{++} ions in the from of a water-soluble zinc salt composition and/or product in the rinse liquor of an automatic dishwashing appliance. In one embodiment, a water-soluble zinc salt may be present in an amount from 0.01% to 70%, by weight of the composition. In another non-limiting embodiment, the water-soluble zinc salt is used directly as the raw

material in the rinse aid composition and/or provided as an additive compound or product that is added along with other component to form the rinse aid composition.

Aluminum Salt

[0020] Any suitable water-soluble salt of aluminum may be used to make the rinse aid compositions.

[0021] Suitable water-soluble aluminum salts include, but are not limited to aluminum acetate, aluminum ammonium sulfate, aluminum chlorate, aluminum chloride, aluminum chlorohydrate, aluminum diformate, aluminum formoacetate, aluminum monostearate, aluminum lactate, aluminum nitrate, aluminum sodium sulfate, aluminum sulfate, aluminum stearate, aluminum tartrate, aluminum triformate, and mixtures thereof.

[0022] In one non-limiting embodiment, the rinse aid composition may be designed to deliver from 0.1% to 20% by weight of Al^{+++} ions in the form of a water-soluble aluminum salt composition and/or product in the rinse liquor of an automatic dishwashing appliance. In another non-limiting embodiment, the water-soluble aluminum salt is used directly as the raw material in the rinse aid composition and/or provided as ah additive compound or product that is added along with other components to form the rinse aid composition.

Magnesium Salt

[0023] Any suitable water-soluble salt of magnesium may be used to make the rinse aid composition.

[0024] Water-soluble magnesium salts include, but are not limited to: magnesium acetate, magnesium acetylacctonate, magnesium ammonium phosphate, magnesium benzoate, magnesium biophosphate, magnesium borate, magnesium borocitrate, magnesium bromate, magnesium bromide, magnesium calcium chloride, magnesium chlorate, magnesium chloride, magnesium citrate, magnesium dichromate, magnesium fluosilicate, magnesium formate, magnesium gluconate, magnesium glycerophosphate, magnesium lauryl sulfate, magnesium nitrate, magnesium perchlorate, magnesium permanganate, magnesium salicylate, magnesium stannate, magnesium stannide, magnesium sulfate, and mixtures thereof.

[0025] In one non-limiting embodiment, the rinse aid composition may be designed to deliver from 0.1% to 20% by weight of Mg^{++} ions in the form of a water-soluble magnesium salt composition and/or product in the rinse liquor of an automatic dishwashing appliance. In another non-limiting embodiment, the water-soluble magnesium salt is used directly as the raw material in the rinse aid composition and/or provided as an additive compound or product that is added along with other components to form the rinse aid composition.

Calcium Salt

[0026] Any suitable water-soluble salt of calcium may be used to make the rinse aid composition.

[0027] Water-soluble calcium salts include, but are not limited to: calcium acetate, calcium acetylsalicylate, calcium acrylate, calcium ascorbate, calcium borate, calcium bromate, calcium bromide, calcium chlorate, calcium chloride, calcium cyclamate, calcium dehydroacetate, calcium dichromate, calcium disodium edetate, calcium ethylhexoate, calcium formate, calcium gluconate, calcium iodate, calcium nitrite, calcium pantothenate, calcium perborate, calcium perchlorate, calcium permanganate, calcium propionate, calcium tartate, and calcium thiocynnate, and mixtures thereof.

[0028] In one non-limiting embodiment, the rinse aid composition may be designed to deliver from 0.1% to 20% by weight of Ca^{++} ions in the form of a water-soluble calcium salt composition and/or product in the rinse liquor of an automatic dishwashing appliance. In another non-limiting embodiment, the water-soluble calcium salt is used directly as the raw material in the rinse aid composition and/or provided as an additive compound or product that is added along with other components to form the rinse aid composition.

Other Water-Soluble Metal Salts

[0029] Any other suitable water-soluble metal salt may be used to make the rinse aid composition.

[0030] These other water-soluble metal salts may include at least one salt selected from the group consisting of lanthanum, tin, gallium, strontium, titanium, and combinations thereof which may be delivered and/or formulated to the rinse liquor in an automatic dishwashing appliance in the same amount as disclosed above.

[0031] In one non-limiting embodiment, the rinse aid composition may be designed to deliver from 0.1% to 20% by weight of these other metal ions in the form of an other water-soluble metal salt composition and/or product in the rinse liquor of an automatic dishwashing appliance. In another non-limiting embodiment, any other water-soluble metal salt is used directly as the raw material in the rinse aid composition and/or provided as an additive compound or product that is added along with other components to form the rinse aid composition.

Acid

[0032] Any suitable organic and/or inorganic acid may be used in the rinse aid compositions and/or products. Some suitable acids include, but are not limited to: acetic acid, aspartic acid, benzoic acid, boric acid, bromic acid, citric acid, formic acid, gluconic acid, glutamic acid, hydrochloric acid, lactic acid, malic acid, nitric acid, sulfamic acid, sulfuric acid, tartaric acid, and mixtures thereof.

[0033] In the case of a liquid rinse aid composition, adding an acid to the rinse aid composition enables the water-soluble metal salt to at least partially dissolve, and alternatively to fully dissolve, in the composition. The acid also helps to at least partially reduce the precipitation on hard surfaces during the rinse cycle. The acid may be also needed to stabilize the liquid rinse aid composition against precipitation in the product prior to use.

[0034] In the case of a solid rinse aid composition, adding an acid to the rinse aid composition enables the water-soluble metal salt, once released, to at least partially dissolve, and alternatively to fully dissolve, quickly in the wash and/or rinse liquor of an automatic dishwashing appliance so as to prevent insoluble material from forming and/or from depositing onto hard surfaces, such as on flatware, glasses, dishes and/or components inside the automatic dishwashing appliance itself.

[0035] Acids used for in-situ preparation of water-soluble metal salts must be non-precipitating acids. Certain acids will not result in precipitation of the water-soluble metal salt in the rinse aid composition and/or product itself or in rinse liquor of the automatic dishwashing appliance during the rinse cycle. For example, nitric acid, hydrochloric acid, and mixtures thereof, are typically non-precipitation acids. Conversely, other acids, like phosphoric acid, citric acid, and mixtures thereof, are precipitating acids, which may result in precipitation of an insoluble metal salt in the rinse aid composition and/or product itself. These precipitating acids cannot be used in the in-situ water-soluble metal salt preparation process itself. However, a low level of a precipitating acid may be added after the completion of the in-situ water-soluble metal salt preparation process.

[0036] The amount of acid needed in the in-situ water-soluble metal salt preparation process may, for example, be determined stoichimetrically using the formula:

$$2\ H_x\ A + X\ ZnO \rightarrow X\ Z_n\ A_{2/x} + X\ H_2O$$

wherein A is an organic and/or an inorganic acid, and x is an integer that varies from 1 to 2. Suitable acids are present in an rinse aid compositions and/or products in the range from 0.01% to 25%, alternatively from 0.5% to 20%, and alternatively from 1% to 10%, by weight of the composition.

[0037] In one non-limiting embodiment, an acid used in the in-situ water-soluble metal salt preparation process may be selected from the group consisting of acetic acid, formic acid, gluconic acid, glutamic acid, hydrochloric acid, malic acid, nitric acid, sulfuric acid, and mixtures thereof, by weight of the mixture may be used.

pH

[0038] The rinse aid composition may be formulated within any suitable acidic pH range. The pH is measured at a 10% concentration in an aqueous solution for any form of the rinse aid composition.

[0039] Suitable pHs range from 1 to less than 5, alternatively from 1 to 4, and alternatively from 1 to 3. A lower pH range will tend to reduce incompatibility and negative interaction of the rinse aid composition with existing commercial rinse aid product residues left in the rinse aid dispenser reservoir of the automatic dishwashing appliance prior to use.

[0040] In one non-limiting embodiment, the pH of the rinse aid composition may be in the range of from 1 to less than 5.

Nonionic Surfactant

[0041] Any suitable non-ionic surfactant in an amount of from 0.01% to about 60% by weight may be used to make the rinse aid composition. Suitable non-ionic surfactants include, but are not limited to, low foaming nonionic surfactants (LFNIs). LFNIs are most typically used in automatic dishwashing compositions on account of the improved water-sheeting action (especially from glassware), which they confer to the rinse aide product. They also may encompass non-silicone, phosphate or nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

[0042] In one non-limiting embodiment, an LFNI may include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene / polyoxyethylene / polyoxypropylene reverse block polymers. Suitable block polyoxyethylene-polyoxypropylene polymeric compounds that meet the requirements may include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine, and mixtures thereof, as initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom,

such as C_{12-18} aliphatic alcohols, do not generally provide satisfactory suds control in rinse aid compositions. However, certain of the block polymer surfactant compounds designated as PLURONIC® and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in rinse aide compositions.

[0043] In another non-limiting embodiment, the LFNI may contain from 40% to 70% of a polyoxypropylene / polyoxyethylene / polyoxypropylene block polymer blend comprising 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and 25%, by weight of the blend, of a block co-polymer of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane and containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylolpropane.

[0044] In another non-limiting embodiment, the rinse aid composition may include the use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol fraction of the LFNI comprising from 20% to 80%, alternatively from 30% to 70%, of the total LFNI.

[0045] The LFNI can optionally contain propylene oxide in an amount up to about 15% by weight. Other alternative LFNI surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty.

[0046] The LFNI may be an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from 8 to 20 carbon atoms, excluding cyclic carbon atoms, with from 6 to 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis.

[0047] The LFNI may be derived from a straight chain fatty alcohol containing from 16 to 20 carbon atoms (C_{16}-C_{20} alcohol), alternatively a C_{18} alcohol, condensed with an average of from 6 to 15 moles, alternatively from 7 to 12 moles, and alternatively from 7 to 9 moles of ethylene oxide per mole of alcohol. Alternatively the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

[0048] Suitable for use as an LFNI in the rinse aid compositions are those LFNIs having relatively low cloud points and high hydrophilic-lipophilic balance (HLB). Cloud points of 1% solutions in water are typically below 32°C and alternatively lower, e.g., 0°C, for optimum control of sudsing throughout a full range of water temperatures.

[0049] An LFNI may, for example, be present in an amount in the range of from 0.01% to 60% by weight, alternatively from 0.01% to 50%, and alternatively from 0.01% to 40% by weight of the rinse aid composition.

[0050] In one non-limiting embodiment, the rinse aid composition comprises from 0.01% to 60% by weight of the composition of a low-foarning nonionic surfactant having a cloud point below 30 °C. In another non-limiting embodiment, the surfactant may be a low cloud point nonionic surfactant selected from the group consisting of $C_{9/11}EO_8$-cyclohexyl acetal alkyl capped nonionic, $C_{11}EO_7$-n-butyl acetal, $C_{9/11}EO_8$-2-ethylhexyl acetal, $C_{11}EO_8$-pyranyl, alcohol alkoxylate, and mixtures thereof.

[0051] In another non-limiting embodiment, the LFNI may include a C_{18} alcohol polyethoxylate, having a degree of ethoxylation of 8, commercially available SLF18® from Olin Corp™. Any biodegradable LFNI having the melting point properties discussed herein above, and mixtures thereof.

Dispersant Polymer

[0052] The dispersant polymer is a low molecular weight modified polyacrylate copolymer, Such copolymers contain as monomer units: a) from 90% to 10%, alternatively from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, alternatively from 20% to 80% by weight of substituted acrylic monomer or its salt and have the general formula:

$$-[(C(R^2)C(R^1)(C(O)OR^3)]-$$

wherein the incomplete valencies inside the square braces are hydrogen and at least one of the substituents R^1, R^2 or R^3, alternatively R^1 or R^2, is a 1 to 4 carbon alkyl or hydroxyalkyl group, R^1 or R^2 can be a hydrogen and R^3 can be a hydrogen or alkali metal salt. In one alternative, a substituted acrylic monomer may be used wherein R^1 is methyl, R^2 is hydrogen and R^3 is sodium.

[0053] Dispersant polymers are useful in rinse aid compositions because they provide improved filming performance, improved surface wetting, and improved particulate suspension and/or dispersion.

[0054] Suitable polymers are described in U.S. Pat. No. 4,379,080 (Murphy), issued Apr. 5, 1983. These polymers inhibit the deposition of calcium carbonate or magnesium silicate on dishware. Unsaturated monomeric acids that can be polymerized to form suitable dispersant polymers include acrylic acid.

[0055] In one non-limiting embodiment, the rinse aid composition may include a dispersant polymer comprising one or more homopolymer, copolymer, terpolymer, and mixtures thereof.

[0056] Substantially non-neutralized forms of the polymer may be used in the rinse aid compositions. The molecular weight of the polymer can vary ever a wide range, for instance from 1000 to 500,000 alternatively from 1000 to 250,000.

If the rinse aid composition is for use in North American automatic dishwashing appliances, it may be desirable for the molecular weight of the polymer to range from 1000 to 5,000.

[0057] The low molecular weight polyacrylate dispersant polymer alternatively has a molecular weight of less than 15,000, alternatively from 500 to 10,000, alternatively from 1,000 to 5,000. Alternatively, the polyacrylate copolymer for use herein may have a molecular weight of 3500 and is the non-neutralized form of the polymer comprising 70% by weight acrylic acid and 30% by weight methacrylic acid.

[0058] Other suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents 4,530,766.

[0059] In another non-limiting embodiment, the dispersant polymers may also include polyacrylates with an average molecular weight of from 1,000 to 10,000.

[0060] When present, a dispersant polymer in the rinse aid composition is compatible with other components. A dispersant polymer may, for example, be present in an amount from 0.01% to 25%, alternatively from 0.5% to 20%, and alternatively from 1% to 7% by weight of the rinse aid composition.

Perfume

[0061] Any suitable perfume in any suitable amount may be used to make the rinse aid composition. Perfumes are useful for improved odor profiles of the water-soluble metal salt containing rinse aid composition, as well as, during the automatic dishwashing operation.

[0062] A perfume may, for example, be present in an amount from 0.01% to 5%, alternatively from 0.1% to 3%, and alternatively from about 0.1% to about 2% of a perfume composition. Suitable perfumes used in this rinse aid composition may be classified as non-blooming as well as blooming perfumes.

[0063] The following references disclose a wide variety of perfumes U.S. Pat. No. 3,983,079; U.S. Pat. No. 4,105,573; U.S. Pat. No. 4, 219,436; U.S. Pat. No. 4,339,356; U.S. Pat. No. 4,515,705; U.S. Pat. No. 4,714,562; U.S. Pat. No. 4,740,327; U.S. Pat. No. 4,933,101; U.S. Pat. No, 5,061,393; U.S. Pat. No. 5,066,419; U.S. Pat. No. 5,154,842; U.S. Pat, No. 5,232,613; U.S. Pat. No. 5,500,154; U.S. Pat. No. 5,670,475; U.S. Pat. No. 6,143,707; and U.S. Pat. No. 6,194,362.

Carrier Medium

[0064] Any suitable carrier medium in any suitable amount may be used to make the rinse aid composition. Suitable carrier mediums include both liquids and solids. Several non-limiting examples of types of carrier mediums are provided by way of explanation, and not by way of limitation. In one example, the rinse aid composition can be provided in the form of an aqueous liquid in a container. In another example, the rinse aid composition may exist in a solid form in a container and the solid could be dissolved with water. In another example, the rinse aid composition can be provided in the form of a combination of both a liquid and a solid that can be diluted or dissolved with water. In one non-limiting embodiment, the form of the rinse aid composition can be a dry powder, granule or tablet, encapsulated particles, and combinations thereof.

[0065] One suitable carrier medium may be water, which can be distilled, deionized, or tap water. Water may be preferred due to its low cost, availability, safety, and compatibility. In other non-limiting embodiments the carrier medium may be tap water.

[0066] In one non-limiting embodiment in which the carrier medium may be aqueous, at least some of the aqueous carrier may be purified beyond the treatment it received to convert it to tap water (that is, the tap water may be post-treated, e.g., deionized or distilled). In yet another non-limiting embodiment at least some of the carrier may be hard water having a hardness of at least 3.3 mM (Calcium:Magnesium = 3:1).

[0067] Optionally, in addition to water, the carrier can contain a low molecular weight organic solvent that may be highly soluble in water, e.g., ethanol, methanol, propanol, isopropanol and the like, and mixtures thereof. Low molecular weight alcohols can allow the treated hard metal surface to dry faster. The optional water-soluble low molecular weight solvent can also be used at a level of up to 50%, typically from 0.1% to 25%, alternatively from 2% to 15%, alternatively from 5% to 10%, by weight of the suitable carrier medium.

[0068] Factors that need to be considered when a high level of solvent is combined with the suitable carrier medium are odor, flammability, dispersancy and environment impact.

[0069] Rinse aid compositions can also be in a "concentrated form", in such case, the concentrated liquid rinse aid composition according one non-limiting embodiment will contain a lower amount of a suitable carrier medium, compared to conventional liquid rinse aid compositions. For example, the suitable carrier medium content of the concentrated system may be present in an amount from 30% to 99.99% by weight of the rinse aid composition. The dispersant content of the concentrated system rinse aid composition may be present in an amount from 0,001% to 10 % by weight of the rinse aid composition.

Binder

[0070] The solid rinse aid compositions may also contain any suitable binder in any suitable amount. The binding agent of the solid rinse aid composition holds the dry components together in a single mass. The binding agent may comprise any material which is relatively high melting and which will maintain product integrity,

[0071] Suitable binders include, but are not limited to, materials such as nonionic surfactants, polyethylene glycols, anionic surfactants, film forming polymers, fatty acids, and mixtures thereof, wherein the binder does not melt below 40°C, as disclosed in U.S. Patent 4,486,327, Murphy et al, issued December 4, 1984. In certain embodiments, certain binders include alkali metal phosphates, fatty amides, and combinations thereof.

[0072] Suitable binders may, for example, be optionally incorporated in the rinse aid composition at a level of from 0.05% to 98%, alternatively from 0.05% to 70%, alternatively from 0.05% to 50%, alternatively from 0.05% to 30%, alternatively from 0.05% to 10%, and alternatively from 0.1% to 5% by weight of the total composition. Filler materials can also be present in the rinse aid composition. These may include sucrose, sucrose esters, alkali metal chlorides or sulfates, in amounts from 0.001% to 60%, and alternatively from 5% to 30% of the composition.

Hydrotrope

[0073] Any suitable hydrotrope in any suitable amount may be used to make the rinse aid composition. Suitable hydrotropes include, but are not limited to, sodium benzene sulfonate, sodium toluene sulfonate, sodium cumene sulfonate, and mixtures thereof.

[0074] The following references disclose a wide variety of suitable hydrotropes: U.S. Pat. No. 6,130,194; U.S. Pat. No. 5,942,485; U.S. Pat, No. 5,478,503; U.S. Pat. No. 5,478,502; U.S. Pat. No. 6,482,786; U.S. Pat. No. 6,218,345; U.S. Pat. No. 6,191,083; U.S. Pat. No, 6,162,778; U.S, Pat. No. 6,152,152; U.S. Pat. No. 5,540,865; U.S. Pat, No. 5,342,549; U.S. Pat. No. 4,966,724; U.S. Pat. No. 4,438,024; and U.S. Pat. No. 3,933,671.

PRODUCT FORM

[0075] The rinse aid composition may be used in any variety of product forms, including, but not limited to, liquid, gel, solid, granular, powder, and combinations thereof. In one non-limiting embodiment, the rinse aid composition may be formulated as a solid to deliver a water-soluble metal salt to the rinse without excessive precipitation. In another non-limiting embodiment, the rinse aid composition comprising water-soluble metal salt in the form of a solid, which could be designed to delay release of the water-soluble metal salt until the rinse cycle,

[0076] The rinse aid composition in any physical form (e.g. liquid, gel, solid, granular, powder, and combinations thereof) may be packaged in a water-soluble or water dispersible pouch, and combinations thereof, to deliver the water-soluble metal salt to the rinse liquor. The rinse aid composition can be in the form of a unit dose, which allows for the controlled release (for example delayed, sustained, triggered or slow release) of the water-soluble metal salt during the rinse cycle of an automatic dishwashing appliance.

[0077] Single- and multi-compartment water-soluble pouches may be suitable for use. In the case of additive and multi-component products, the rinse aid compositions do not need to be in the same physical form. In another non-limiting embodiment, the rinse aid composition may be formulated in a multi-compartmental pouch so that negative interactions with other rinse aid components are minimized.

[0078] In yet another embodiment, rinse aid compositions suitable for use can be dispensed from any suitable device, such as bottles (pump assisted bottles, squeeze bottles), paste dispensers, capsules, multi-compartment bottles, multi-compartment capsules, and single- and multi-compartment water-soluble pouches, and combinations thereof.

[0079] In another non-limiting embodiment, the rinse aid composition can be in the form of a unit dose, which allows for the controlled release (for example delayed, sustained, triggered or slow release) of the water-soluble metal salt during the rinse cycle of an automatic dishwashing appliance. In unit dose forms, for example, the rinse aid composition may be a solid, granular, powder, liquid, gel, and combinations thereof, and may be provided as a tablet or contained in a single or multi-compartment water-soluble pouch.

Claims

1. A rinse aid composition for reducing metal corrosion and rust formation **characterized by** comprising:

a) from about 0.01% to about 70% by weight of at least one water-soluble metal salt;
b) from about 0.01% to about 25% by weight of an acid;
c) from about 0.01% to about 60% by weight of a non-ionic surfactant;

d) a dispersant polymer, and
e) optionally at least one component selected from the group consisting of acid, dispersant polymer, perfume, hydrotrope, binder, carrier medium, antibacterial active, dye, and mixtures thereof;

wherein said rinse aid composition has a pH of less than about 5 when measured at a 10% concentration in an aqueous solution and wherein said at least one water-soluble metal salt comprises zinc and wherein said water-soluble zinc salt is selected from the group consisting of zinc acetate, zinc chloride, zinc gluconate, zinc formate, zinc malate, zinc nitrate, zinc sulfate, and mixtures thereof and wherein said dispersant polymer is a low molecular weight modified polyacrylate copolymer, wherein said copolymer contains as monomer units:

a) from about 90% to about 10% by weight acrylic acid or its salts, and
b) from about 10% to about 90% by weight of a substituted acrylic monomer or its salt and have the general formula:

$$-[(C(R^2)C(R^1)(C(O)OR^3)]-$$

wherein the incomplete valencies inside the square braces are hydrogen and at least one of the substituents R^1, R^2 or R^3 is a 1 to 4 carbon alkyl or hydroxyalkyl group, and wherein R^1 or R^2 can be a hydrogen and R^3 can be a hydrogen or alkali metal salt.

2. A rinse aid composition according to Claim 1, wherein said rinse aid composition delivers from about 0.01 mM to about 10 mM, alternatively from about 0.02 mM to about 5 mM of said at least one water-soluble metal salt in the rinse liquor.

3. A rinse aid composition according to any preceding claim, wherein said acid is selected from the group consisting of organic, inorganic, and mixtures thereof.

4. A rinse aid composition according to any preceding claim, wherein said acid is selected from the group consisting of acetic acid, aspartic acid, benzoic acid, boric acid, bromic acid, citric acid, formic acid, gluconic acid, glutamic acid, hydrochloric acid, lactic acid, malic acid, nitric acid, sulfamic acid, sulfuric acid, tartaric acid, and mixtures thereof.

5. A rinse aid composition according to any preceding claim, wherein said pH is in the range of from about 1 to about 4.

6. A rinse aid composition according to any preceding claim, wherein said dispersant polymer comprises at least one or more homopolymer, copolymer, terpolymer, and mixtures thereof.

7. A rinse aid composition according to any preceding claim, wherein said dispersant polymer is a low molecular weight polyacrylate dispersant polymer having a molecular weight of less than about 15,000, alternatively from about 500 to about 10,000, and alternatively about 3500, and is the non-neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

8. A rinse aid composition according to any preceding claim, wherein said incomplete valencies inside the square braces are hydrogen and at least one of the substituents R^1 or R^2 is a 1 to 4 carbon alkyl or hydroxyalkyl group

9. A rinse aid composition according to any preceding claim, wherein said dispersant polymer is a substituted acrylic monomer, and wherein R^1 is methyl, R^2 is hydrogen and R^3 is sodium.

10. A rinse aid composition according to Claim 1, wherein said composition further comprises at least one component selected from the group consisting of hydrotrope, binder, dispersant polymer, perfume, carrier medium, antibacterial active, dye, and mixtures thereof.

Patentansprüche

1. Spülhilfsmittelzusammensetzung zum Reduzieren von Metallkorrosion und Rostbildung, **dadurch gekennzeichnet, dass** sie Folgendes umfasst:

a) von etwa 0,01 Gew.-% bis etwa 70 Gew.-% mindestens ein wasserlösliches Metallsalz;
b) von etwa 0,01 Gew.-% bis etwa 25 Gew.-% eine Säure;
c) von etwa 0,01 Gew.-% bis etwa 60 Gew.-% ein nichtionisches Tensid;
d) ein Dispergierpolymer und
e) wahlweise mindestens einen Bestandteil, ausgewählt aus der Gruppe bestehend aus Säure, Dispergierpolymer, Duftstoff, Hydrotropikum, Bindemittel, Trägermedium, antibakteriellem Wirkstoff, Farbstoff und Mischungen davon;

wobei die Spülhilfsmittelzusammensetzung einen pH-Wert von weniger als etwa 5 aufweist, wenn bei einer Konzentration von 10 % in einer wässrigen Lösung gemessen wird, und wobei das mindestens eine wasserlösliche Metallsalz Zink umfasst, und wobei das wasserlösliche Zinksalz ausgewählt ist aus der Gruppe bestehend aus Zinkacetat, Zinkchlorid, Zinkgluconat, Zinkformiat, Zinkmalat, Zinknitrat, Zinksulfat und Mischungen davon, und wobei das Dispergierpolymer ein niedermolekulares, modifiziertes Polyacrylatcopolymer ist, wobei das Copolymer Folgendes als Monomereinheiten enthält:

a) von etwa 90 Gew.-% bis etwa 10 Gew.-% Acrylsäure oder deren Salze und
b) von etwa 10 Gew.-% bis etwa 90 Gew.-% ein substituiertes Acrylmonomer oder dessen Salz, und mit der allgemeinen Formel:

$$-[(C(R^2)C(R^1)(C(O)OR^3)]-$$

wobei die unvollständigen Valenzen innerhalb der eckigen Klammern Wasserstoff sind und mindestens einer der Substituenten R^1, R^2 oder R^3 eine 1 bis 4 Kohlenstoffe enthaltende Alkyl- oder Hydroxyalkylgruppe ist, und wobei R^1 oder R^2 ein Wasserstoff sein kann und R^3 ein Wasserstoff oder ein Alkalimetallsalz sein kann.

2. Spülhilfsmittelzusammensetzung nach Anspruch 1, wobei die Spülhilfsmittelzusammensetzung von etwa 0,01 mM bis etwa 10 mM, als Alternative von etwa 0,02 mM bis etwa 5 mM, von dem mindestens einen wasserlöslichen Metallsalz in die Spülflotte abgibt.

3. Spülhilfsmittelzusammensetzung nach einem der vorstehenden Ansprüche, wobei die Säure ausgewählt ist aus der Gruppe bestehend aus organischen, anorganischen und Mischungen davon.

4. Spülhilfsmittelzusammensetzung nach einem der vorstehenden Ansprüche, wobei die Säure ausgewählt ist aus der Gruppe bestehend aus Essigsäure, Asparaginsäure, Benzoesäure, Borsäure, Bromsäure, Citronensäure, Ameisensäure, Gluconsäure, Glutaminsäure, Salzsäure, Milchsäure, Äpfelsäure, Salpetersäure, Sulfaminsäure, Schwefelsäure, Weinsäure und Mischungen davon.

5. Spülhilfsmittelzusammensetzung nach einem der vorstehenden Ansprüche, wobei der pH-Wert im Bereich von etwa 1 bis etwa 4 liegt.

6. Spülhilfsmittelzusammensetzung nach einem der vorstehenden Ansprüche, wobei das Dispergierpolymer mindestens ein oder mehrere Homopolymere, Copolymere, Terpolymere und Mischungen davon umfasst.

7. Spülhilfsmittelzusammensetzung nach einem der vorstehenden Ansprüche, wobei das Dispergierpolymer ein niedermolekulares Polyacrylat-Dispergierpolymer mit einem Molekulargewicht von weniger als etwa 15.000, als Alternative von etwa 500 bis etwa 10.000 und als Alternative etwa 3.500 ist, und die unneutralisierte Form des Polymers ist, die etwa 70 Gew.-% Acrylsäure und etwa 30 Gew.-% Methacrylsäure umfasst.

8. Spülhilfsmittelzusammensetzung nach einem der vorstehenden Ansprüche, wobei die unvollständigen Valenzen innerhalb der eckigen Klammern Wasserstoff sind und mindestens einer der Substituenten R^1 oder R^2 eine 1 bis 4 Kohlenstoffe enthaltende Alkyl- oder Hydroxyalkylgruppe ist.

9. Spülhilfsmittelzusammensetzung nach einem der vorstehenden Ansprüche, wobei das Dispergierpolymer ein substituiertes Acrylmonomer ist, und wobei R^1 Methyl ist, R^2 Wasserstoff ist und R^3 Natrium ist.

10. Spülhilfsmittelzusammensetzung nach Anspruch 1, wobei die Zusammensetzung ferner mindestens einen Bestandteil umfasst, ausgewählt aus der Gruppe bestehend aus Hydrotropikum, Bindemittel, Dispergierpolymer, Duftstoff,

Trägermedium, antibakteriellem Wirkstoff, Farbstoff und Mischungen davon.

Revendications

1. Composition d'aide au rinçage destinée à réduire la corrosion métallique et la formation de rouille, **caractérisée en ce qu'**elle comprend :

   a) d'environ 0,01 % à environ 70 % en poids d'au moins un sel métallique hydrosoluble ;
   b) d'environ 0,01 % à environ 25 % en poids d'un acide ;
   c) d'environ 0,01 % à environ 60 % en poids d'un tensioactif non ionique ;
   d) un polymère dispersant, et
   e) éventuellement, au moins un composant choisi dans le groupe constitué d'acide, polymère dispersant, parfum, hydrotrope, liant, milieu véhiculaire agent actif antibactérien, colorant et des mélanges de ceux-ci ;

   où ladite composition d'aide au rinçage a un pH inférieur à environ 5 quand elle est mesurée à une concentration de 10 % dans une solution aqueuse et où ledit au moins un sel métallique hydrosoluble comprend du zinc et où ledit sel de zinc hydrosoluble est choisi dans le groupe constitué d'acétate de zinc, chlorure de zinc, gluconate de zinc, formiate de zinc, malate de zinc, nitrate de zinc, sulfate de zinc et mélanges de ceux-ci et où ledit polymère dispersant est un copolymère de polyacrylate modifié à bas poids moléculaire, ledit copolymère contenant, en tant qu'unités monomères :

   a) d'environ 90 % à environ 10 % en poids d'acide acrylique ou de ses sels, et
   b) d'environ 10 % à environ 90 % en poids d'un monomère acrylique substitué ou de son sel et ayant la formule générale :

   $$-[(C(R^2)C(R^1)(C(O)OR^3)]-$$

   dans laquelle les valences incomplètes à l'intérieur des crochets sont l'hydrogène et au moins l'un des substituants R^1, R^2 ou R^3 est un groupe alkyle ou hydroxyalkyle de 1 à 4 atomes de carbone, R^1 ou R^2 pouvant être un hydrogène et R^3 pouvant être un hydrogène ou un sel de métal alcalin.

2. Composition d'aide au rinçage selon la revendication 1, ladite composition d'aide au rinçage délivrant d'environ 0,01 mM à environ 10 mM, alternativement d'environ 0,02 mM à environ 5 mM dudit au moins un sel métallique hydrosoluble dans la liqueur de rinçage.

3. Composition d'aide au rinçage selon l'une quelconque des revendications précédentes, dans laquelle ledit acide est choisi dans le groupe constitué de substance organique, substance inorganique, et des mélanges de ceux-ci.

4. Composition d'aide au rinçage selon l'une quelconque des revendications précédentes, dans laquelle ledit acide est choisi dans le groupe constitué d'acide acétique, acide aspartique, acide benzoïque, acide borique, acide bromique, acide citrique, acide formique, acide gluconique, acide glutamique, acide chlorhydrique, acide lactique, acide malique, acide nitrique, acide sulfamique, acide sulfurique, acide tartrique et des mélanges de ceux-ci.

5. Composition d'aide au rinçage selon l'une quelconque des revendications précédentes, dans laquelle ledit pH se trouve dans la plage allant d'environ 1 à environ 4.

6. Composition d'aide au rinçage selon l'une quelconque des revendications précédentes, dans laquelle ledit polymère dispersant comprend au moins un ou plusieurs homopolymères, copolymères, terpolymères, et des mélanges de ceux-ci.

7. Composition d'aide au rinçage selon l'une quelconque des revendications précédentes, dans laquelle ledit polymère dispersant est un polymère dispersant polyacrylate à bas poids moléculaire ayant un poids moléculaire inférieur à environ 15 000, alternativement d'environ 500 à environ 10 000 et en alternativement d'environ 3 500, et se trouve sous la forme non neutralisée du polymère comprenant environ 70 % en poids d'acide acrylique et environ 30 % en poids d'acide méthacrylique.

8. Composition d'aide au rinçage selon l'une quelconque des revendications précédentes, dans laquelle lesdites va-

lences incomplètes à l'intérieur des crochets sont l'hydrogène et au moins l'un des substituants R^1 ou R^2 est un groupe alkyle ou hydroxyalkyle de 1 à 4 atomes de carbone

9. Composition d'aide au rinçage selon l'une quelconque des revendications précédentes, dans laquelle ledit polymère dispersant est un monomère acrylique substitué, et dans laquelle R^1 est un méthyle, R^2 est l'hydrogène et R^3 est le sodium.

10. Composition d'aide au rinçage selon la revendication 1, dans laquelle ladite composition comprend en outre au moins un composant choisi dans le groupe constitué d'hydrotope, liant, polymère dispersant, parfum, moyen de transport, agent actif antibactérien, colorant et des mélanges de ceux-ci.

REFERENCES CITED IN THE DESCRIPTION

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