(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
05 March 2020 (05.03.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/043844 A1

(51) International Patent Classification:
C11D 3/28 (2006.01) *C11D 17/00* (2006.01)
C11D 3/39 (2006.01) *C11D 17/04* (2006.01)
C11D 3/48 (2006.01)

(21) International Application Number:
PCT/EP2019/073126

(22) International Filing Date:
29 August 2019 (29.08.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1814188.7 31 August 2018 (31.08.2018) GB

(71) Applicant: **RECKITT BENCKISER FINISH B.V.** [NL/NL]; Siriusdreef 14, 2132WT Hoofddorp (NL).

(72) Inventors: **HAHN, Karlheinz Ulrich**; Reckitt Benckiser Global R&D GmbH, Robert-Koch-Str. 1, 69115 Heidelberg (DE). **HÜTTMANN, Gerd-Erich**; Reckitt Benckiser Global R&D GmbH, Robert-Koch-Str. 1, 69115 Heidelberg (DE). **MÜLLER-LEIFHEIT, Rainer**; Reckitt Benckiser Global R&D GmbH, Robert-Koch-Str. 1, 69115 Heidelberg (DE). **MUENTZENBERGER, Addie**; Reckitt Benckiser Global R&D GmbH, Robert-Koch-Str. 1, 69115 Heidelberg (DE). **ROTH, Torsten**; Reckitt Benckiser Global R&D GmbH, Robert-Koch-Str. 1, 69115 Heidelberg (DE).

(74) Agent: **LESLIE, Edward** et al.; Reckitt Benckiser Corporate Services Limited, Legal Department - Patents Group, Dansom Lane, Hull HU8 7DS (GB).

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

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

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

(54) Title: AUTOMATIC DISHWASHING PRODUCT

(57) Abstract: An automatic dishwashing product comprising a bleaching agent and 5-methyl-1H-benzotriazole.

WO 2020/043844 A1

Automatic dishwashing product

The present disclosure relates to an improved automatic dishwashing product. In particular, the present disclosure relates to the use of a silver/copper corrosion inhibitor in an automatic dishwashing product that is equally effective in inhibiting silver and copper corrosion as existing benzotriazole-based inhibitors while reducing the release of harmful and less biodegradable benzotriazoles into the environment.

A diverse array of compositions designed for use in automatic dishwasher machines is well known, and a consistent and ongoing effort has been made by detergent manufacturers to reduce the tarnishing of silver and copper items and surfaces in the dishwasher. This problem becomes apparent when bleach-containing compositions are employed, and especially those which contain oxygen-bleaching species. The level of tarnishing observed can range from slight discolouration to the formation of a dense black coating on the surface of the silverware or copperware, depending on the formulation and the bleaching agent. The dual challenge in formulating a product is therefore the optimization of the cleaning of bleachable soils while minimizing the occurrence of tarnishing of silverware items.

Existing formulations achieve this through the inclusion of BTA (1H-benzotriazole) and/or TTA (a mixture of 4-methyl-*1H*-benzotriazole and 5-methyl-*1H*-benzotriazole, typically in a ratio of around 40:60). BTA and TTA are both effective at reducing the tarnishing of silverware components in the presence of bleaching agents. However, BTA was found to be toxic to aquatic life and, in addition, is a potential endocrine disruptor (Seeland *et al.*, J. Environ. Sci. Pollut. Res. Int, 2012, 19(5), 1781-1790.

While alternatives to BTA were initially identified, *e.g.* tellurium and selenium dioxide, they have been dismissed due concerns over toxicity. Moreover, reformulation efforts focussing on increased disilicate levels did not yield a viable formula with an improved anti-corrosion profile without exceeding regulatory limits. In the following years, BTA was exchanged by TTA in the formulations due to increasing indications of adverse effects of BTA. However, in recent years several studies have focussed on the adverse effects of TTA on the environment.

Specifically, recent studies in the environmental sciences have highlighted differences in biodegradability between the two constitutional isomers of TTA (Brauch *et. al.,* Water Research and Management, 2011, Vol. 1, No. 1, 17-28). 4-Methyl-*1H*-benzotriazole has been found to be more resistant to conventional wastewater treatment procedures,

resulting in an accumulation of this omnipresent organic micropollutant in the aquatic environment. In contrast, the 5-methyl-*1H*-benzotriazole isomer has been found to be prone to degradation *via* diverse biotransformation pathways and therefore less prevalent in wastewater effluents and of lower environmental relevance (Huntscha *et. al.*, J. Environ. Sci. Technol., 2014, 48, 4435-4443). Because TTA contains a significant quantity of the 4-methyl-*1H*-benzotriazole, existing bleach-containing automatic dishwashing compositions that are effective in minimising silver and copper tarnishing are also harmful to the aquatic environment.

Accordingly, it is one object of the present invention to provide a bleach-containing automatic dishwashing product that is equally effective at inhibiting silver and copper corrosion as existing products while being less harmful to the aquatic environment.

According to a first aspect, the present invention provides an automatic dishwashing product comprising a bleaching agent, 5-methyl-*1H*-benzotriazole and optionally 4-methyl-*1H*-benzotriazole,

wherein when the product comprises 4-methyl-*1H*-benzotriazole, the 5-methyl-*1H*-benzotriazole and the 4-methyl-*1H*-benzotriazole are present in a weight ratio of at least 4:1.

The present inventors have surprisingly found that despite the high structural similarity between 5-methyl-*1H*-benzotriazole and 4-methyl-*1H*-benzotriazole, 5-methyl-*1H*-benzotriazole is more active in inhibiting the silver and copper corrosion effect of bleach-containing automatic dishwashing products. Thus, it is possible to reduce or eliminate the use of 4-methyl-*1H*-benzotriazole in automatic dishwashing products without significantly compromising their ability to inhibit the silver and copper corrosion effect of the bleach, thereby reducing harm to the aquatic environment while achieving equivalent performance characteristics.

According to a second aspect, the present invention provides a method of automatic dishwashing, the method comprising supplying a product to an automatic dishwasher and releasing the product into a wash cycle of the automatic dishwasher, the product comprising a bleaching agent, 5-methyl-*1H*-benzotriazole and optionally 4-methyl-*1H*-benzotriazole,

wherein when the product comprises 4-methyl-*1H*-benzotriazole, the 5-methyl-*1H*-benzotriazole and 4-methyl-*1H*-benzotriazole are present in a weight ratio of at least 4:1.

According to a third aspect, the present invention provides a use of 5-methyl-*1H*-benzotriazole, substantially in the absence of 4-methyl-*1H*-benzotriazole, for reducing corrosion of silver and/or copper by a bleaching agent in an automatic dishwashing process.

The present invention will now be described further. In the following passages different aspects/embodiments of the invention are defined in more detail. Each aspect/embodiment so defined may be combined with any other aspect/embodiment or aspects/embodiments unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

The present invention provides an automatic dishwashing product comprising a bleaching agent. The bleaching agent is preferably selected from the group consisting of an oxygen-releasing bleaching agent, a chlorine-releasing bleaching agent and mixtures of two or more thereof. More preferably, the bleaching agent is or comprises an oxygen-releasing bleaching agent. Oxygen-releasing bleaching agents are known to cause particularly pronounced silver and copper tarnishing, since the release of oxygen can lead to the formation of black silver and copper layers during the cleaning process (especially with low-alkaline formulations providing a pH of less than 11.5 at 1 wt% aqueous solution). Accordingly, the effect of the corrosion inhibitor is most pronounced in products comprising oxygen-releasing bleaching agents.

The bleaching agent may comprise the active bleach species itself or a precursor to that species. Preferably, the bleaching agent is selected from the group consisting of an inorganic peroxide, an organic peracid and mixtures of two or more thereof. The terms “inorganic peroxide” and “organic peracid” encompass salts and derivatives thereof. Inorganic peroxides include percarbonates, perborates, persulphates, hydrogen peroxide and derivatives and salts thereof. The sodium and potassium salts of these inorganic peroxides are suitable, especially the sodium salts. Most preferably, the bleaching agent is selected from the group consisting of sodium percarbonate, ε-phthalimido-peroxy-hexanoic acid (PAP), peracetic acid, potassium peroxymonosulfate (KMPS), and combinations of two or more thereof.

Preferably, the bleaching agent is present in an amount of from 1 to 50 wt% by weight of the automatic dishwashing product, more preferably from 2 to 30 wt%, and most preferably from 5 to 25 wt%. The term “by weight of the automatic dishwashing product”, as used herein, means based on the weight of the cleaning composition(s) and does not

include any packaging or container such as any PVOH film, pouch or capsule housing the cleaning composition(s). All weight percentages expressed herein are by weight of the automatic dishwashing product unless otherwise specified.

The automatic dishwashing product may further comprise one or more bleach activators or bleach catalysts. Any suitable bleach activator may be included, for example TAED, if this is desired for the activation of the bleaching agent. Any suitable bleach catalyst may be used, for example manganese-based bleach catalysts and/or cobalt-based bleach catalysts. Exemplary manganese-based bleach catalysts include manganese acetate, manganese oxalate, or dinuclear manganese complexes such as those described in EP 1741774 A1, the contents of which are incorporated herein by reference. Exemplary cobalt-based bleach catalysts include cobalt complexes such as those described by the formula $[Co(NH_3)_5M]T_y$, wherein cobalt is in the +3 oxidation state, M is a carboxylate ligand and T is one or more counterions present in the number y, wherein y is an integer, preferably 1 or 2, to obtain a charge-balanced salt. Suitable cobalt complexes include those described in WO 1997/000311 A1 and US 5703034 A, the contents of which are incorporated herein by reference. The organic peracids such as perbenzoic acid and peroxycarboxylic acids *e.g.* phthalimidoperoxyhexanoic acid (PAP) do not require the use of a bleach activator or catalyst as these bleaches are active at relatively low temperatures such as about 30°C.

In addition to the bleaching agent, the automatic dishwashing product comprises 5-methyl-*1H*-benzotriazole. The present inventors have found that this isomer is more effective in inhibiting the silver and copper corrosion effect of bleach-containing automatic dishwashing products than 4-methyl-*1H*-benzotriazole. Preferably, the automatic dishwashing product does not comprise 4-methyl-*1H*-benzotriazole. If the product does comprise 4-methyl-*1H*-benzotriazole, the 5-methyl-*1H*-benzotriazole and the 4-methyl-*1H*-benzotriazole are present in a weight ratio of at least 4:1, preferably at least 10:1, more preferably at least 20:1, still more preferably at least 50:1. It is to be understood that this defines the weight ratio of the 5-methyl-*1H*-benzotriazole to the 4-methyl-*1H*-benzotriazole. It is also to be understood that the term “at least 4:1” encompasses 6:1 and 10:1 but not, for example, 4:6.

The present inventors’ finding that 5-methyl-*1H*-benzotriazole is the main active isomer in this context means that the amount of 4-methyl-*1H*-benzotriazole can be reduced or eliminated without compromising the effect on the inhibition of silver and copper corrosion. Thus, the automatic dishwashing products of the present invention are equally

effective as prior art products in terms of their bleaching performance and limited corrosive effect on silver and copper, while reducing harm to the aquatic environment.

While existing automatic dishwashing products employ commercially available BTA and/or TTA (a mixture of 4-methyl-*1H*-benzotriazole and 5-methyl-*1H*-benzotriazole, typically in a ratio of around 40:60), employing the pure of 5-methyl-*1H*-benzotriazole isomer (or a mixture enriched in 5-methyl-1H-benzotriazole) has not yet been described. It was not previously known that mainly the 5-methyl isomer contributes to the corrosion inhibition effect. Accordingly, the preparation of pure 5-methyl-*1H*-benzotriazole, which requires either a stereoselective synthesis of this isomer or, alternatively, a cost-intensive isomer separation step, was not considered until the present inventors' finding.

Preferably, the 5-methyl-*1H*-benzotriazole is present in an amount of from 0.001 to 1 wt% by weight of the automatic dishwashing product, more preferably from 0.01 to 0.5 wt%. If the product comprises 4-methyl-*1H*-benzotriazole, the 4-methyl-*1H*-benzotriazole is preferably present in an amount of less than 0.05 wt%, more preferably less than 0.02 wt%. More preferably, however, the product is free or essentially free of 4-methyl-*1H*-benzotriazole.

If the product comprises *1H*-benzotriazole (BTA) itself, the *1H*-benzotriazole is preferably present in an amount of less than 0.05 wt% by weight of the automatic dishwashing product, more preferably less than 0.02 wt%. More preferably, however, the product is free or substantially free of *1H*-benzotriazole.

Preferably, the bleaching agent and the 5-methyl-*1H*-benzotriazole are present in a weight ratio of from 20:1 to 200:1, more preferably from 50:1 to 150:1. The term "weight ratio" is defined above.

Preferably, the product has a pH of less than 11.5 at 1 wt% aqueous solution at 20 °C, more preferably from 7 to 10.5. In other words, the product preferably has a pH within these ranges when diluted in water in an amount of 1 wt% based on the weight of the aqueous solution that forms. For this definition, the term "product" refers to the cleaning composition(s) and does not include any packaging or container such as any PVOH film, pouch or capsule housing the cleaning composition(s). Preferably, the product is formulated to provide, in use, a cleaning solution having a pH of less than 11.5 at a wash cycle temperature of from 40 to 60 °C, more preferably from 7 to 10.5. In other words, the product is preferably a "low-alkaline" formulation. Low-alkaline formulations containing bleaching agents, especially oxygen-releasing bleaching agents, are known

to be particularly corrosive towards silver and copper. This is because the relatively low pH further shifts the oxidation potentials to favour the formation of black silver and copper layers during the cleaning process. Accordingly, the corrosion inhibitor of the present invention is particularly effective in low-alkaline formulations.

The automatic dishwashing product may comprise a source of acidity or a source of alkalinity, to obtain or/and buffer the desired pH on dissolution. The source of acidity may be any suitable acidic compound, for example a polycarboxylic acid. The source of alkalinity may, for example, be a carbonate or bicarbonate (such as the alkali metal or alkaline earth metal salts). The source of alkalinity may suitably be any suitable basic compound for example any salt of a strong base and a weak acid. When an alkaline composition is desired silicates are amongst the suitable sources of alkalinity. Preferred silicates are sodium silicates such as sodium disilicate, sodium metasilicate and crystalline phyllosilicates. In an embodiment, the product is free of silicates.

Preferably, the automatic dishwashing product further comprises:

one or more builders, and/or
one or more surfactants, and/or
one or more enzymes.

The automatic dishwashing product is preferably an automatic dishwashing detergent product.

Builders

The automatic dishwashing product may comprise a builder (or co-builder). The builder / co-builder may be either a phosphorous-containing builder or a phosphorous-free builder as desired. In many jurisdictions, phosphate builders are banned. Preferably, therefore, the automatic dishwashing product is phosphate-free.

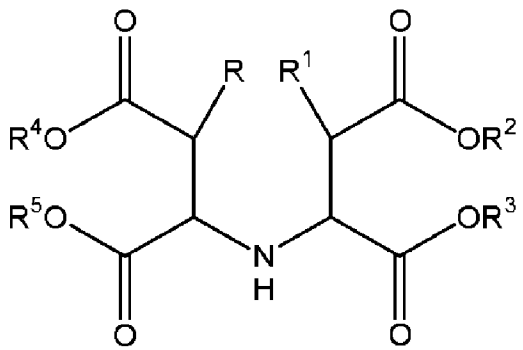
If phosphorous-containing builders are to be used, it is preferred that mono-phosphates, di-phosphates, tri-polyphosphates or oligomeric-polyphosphates are used. The alkali metal salts of these compounds are preferred, in particular the sodium salts. An especially preferred builder is sodium tripolyphosphate (STPP). Conventional amounts of the phosphorous-containing builders may be used typically in the range of from 15 to 60 wt% by weight of the automatic dishwashing product, such as from 20 to 50 wt% or from 25 to 40 wt%.

If phosphorous-free builder is included, it preferably comprises an aminocarboxylate or a citrate. Most preferably, the builder is selected from the group consisting of methylglycine diacetic acid (MGDA), N,N-dicarboxymethyl glutamic acid (GLDA), citrate and combinations of two or more thereof. It is to be appreciated that the terms MGDA GLDA and citrate encompass the free acids as well as salts, esters and derivatives thereof. Preferably, the citrate is trisodium citrate.

Other phosphorous-free builders include succinate based compounds. The terms "succinate based compound" and "succinic acid based compound" are used interchangeably herein. Conventional amounts of the succinate based compounds may be used, typically in the range of from 5 to 80 wt% by weight of the automatic dishwashing product, such as from 15 to 70 wt% or from 20 to 60 wt%. The compounds may be used individually or as a mixture.

Other suitable builders are described in US 6,426,229, which is incorporated by reference herein. Particular suitable builders include; for example, aspartic acid-N-monoacetic acid (ASMA), aspartic acid-N,N-diacetic acid (ASDA), aspartic acid-N-monopropionic acid (ASMP), iminodisuccinic acid (IDA), N-(2-sulfomethyl) aspartic acid (SMAS), N- (2-sulfoethyl)aspartic acid (SEAS), N- (2-sulfomethyl)glutamic acid (SMGL), N-(2- sulfoethyl)glutamic acid (SEGL), N- methyliminodiacetic acid (MIDA), a- alanine-N,N-diacetic acid (a-ALDA), β-alanine-N,N-diacetic acid (β-ALDA), serine-N,N-diacetic acid (SEDA), isoserine-N,N-diacetic acid (ISDA), phenylalanine-N,N-diacetic acid (PHDA), anthranilic acid-N,N- diacetic acid (ANDA), sulfanilic acid-N,N-diacetic acid (SLDA), taurine-N, N-diacetic acid (TUDA) and sulfomethyl-N,N-diacetic acid (SM DA) and alkali metal salts or ammonium salts thereof.

Further preferred succinate compounds are described in US-A-5,977,053, which is incorporated herein by reference, and have the formula:



in which R, R^1, independently of one another, denote H or OH; R^2, R^3, R^4, R^5, independently of one another, denote a cation, hydrogen, alkali metal ions and ammonium ions, ammonium ions having the general formula $R^6R^7R^8R^9N^+$ and R^6, R^7, R^8, R^9, independently of one another, denote hydrogen, alkyl radicals having 1 to 12 C atoms or hydroxyl-substituted alkyl radicals having 2 to 3 C atoms.

Preferred examples include tetrasodium imminosuccinate. Iminodisuccinic acid (IDS) and (hydroxy)iminodisuccinic acid (HIDS) and alkali metal salts or ammonium salts thereof are especially preferred succinate based builder salts. The phosphorous-free co-builder may also or alternatively comprise non-polymeric organic molecules with carboxylic group(s). Builder compounds which are organic molecules containing carboxylic groups include citric acid, fumaric acid, tartaric acid, maleic acid, lactic acid and salts thereof. In particular the alkali or alkaline earth metal salts of these organic compounds may be used, and especially the sodium salts. An especially preferred phosphorous-free builder is sodium citrate. Such polycarboxylates which comprise two carboxyl groups include, for example, water-soluble salts of, malonic acid, (ethylenedioxy)diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid. Such polycarboxylates which contain three carboxyl groups include, for example, water-soluble citrate. Correspondingly, a suitable hydroxycarboxylic acid is, for example, citric acid.

Preferred secondary builders include homopolymers and copolymers of polycarboxylic acids and their partially or completely neutralized salts, monomeric polycarboxylic acids and hydroxycarboxylic acids and their salts, phosphates and phosphonates, and mixtures of such substances. Preferred salts of the abovementioned compounds are the ammonium and/or alkali metal salts, i.e. the lithium, sodium, and potassium salts, and particularly preferred salts is the sodium salts. Secondary builders which are organic are preferred. A polymeric polycarboxylic acid is the homopolymer of acrylic acid. Other suitable secondary builders are disclosed in WO 95/01416, to the contents of which express reference is hereby made. Most preferably, the secondary builder is trisodium citrate.

Preferably the total amount of builder present in the automatic dishwashing product is at least 20 wt% by weight of the automatic dishwashing product, and most preferably at least 25 wt%, preferably in an amount of up to 70 wt%, preferably up 60 wt%, more preferably up to 45 wt%. The actual amount used in the product will depend upon the nature of the builder used. If desired a combination of phosphorous-containing and phosphorous-free builders may be used.

In an especially preferred embodiment, the automatic dishwashing product is phosphate-free and comprises (i) an aminocarboxylate selected from the group consisting of MGDA, GLDA and a combination thereof, and (ii) trisodium citrate, wherein the aminocarboxylate and the trisodium citrate are present in an amount of from 10 to 60 wt% by weight of the automatic dishwashing product.

Surfactants

Surfactants may also be included in the automatic dishwashing product and any of nonionic, anionic, cationic, amphoteric or zwitterionic surface active agents or suitable mixtures thereof may be used. Many such suitable surfactants are described in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detersive Systems", incorporated by reference herein. In general, bleach-stable surfactants are preferred according to the present invention.

In the case of automatic dishwashing products, it is preferred to minimise the amount of anionic surfactant. Preferably the product comprises no more than 2 wt%, no more than 1 wt%, or no, anionic surfactant. Preferably the product comprises no more than 5 wt%, no more than 1 wt %, or no, ionic surfactant of any type. Non-ionic surfactants are especially preferred instead for automatic dishwashing products.

A preferred class of non-ionic surfactants is ethoxylated non-ionic surfactants prepared by the reaction of a monohydroxy alkanol or alkylphenol with 6 to 20 carbon atoms. Preferably the surfactants have at least 12 moles, particularly preferred at least 16 moles, and still more preferred at least 20 moles, such as at least 25 moles, of ethylene oxide per mole of alcohol or alkylphenol. Particularly preferred non-ionic surfactants are the non-ionics from a linear chain fatty alcohol with 16-20 carbon atoms and at least 12 moles, particularly preferred at least 16 and still more preferred at least 20 moles, of ethylene oxide per mole of alcohol.

According to one embodiment of the invention, the non-ionic surfactants additionally may comprise propylene oxide units in the molecule. Preferably these PO units constitute up to 25 wt%, preferably up to 20 wt%, and still more preferably up to 15 wt% by weight of the overall molecular weight of the non-ionic surfactant.

Surfactants which are ethoxylated mono-hydroxy alkanols or alkylphenols, which additionally comprises polyoxyethylene-polyoxypropylene block copolymer units may be

used. The alcohol or alkylphenol portion of such surfactants constitutes more than 30 wt%, preferably more than 50 wt%, more preferably more than 70 wt% by weight of the overall molecular weight of the non-ionic surfactant.

Another class of suitable non-ionic surfactants includes reverse block copolymers of polyoxyethylene and polyoxypropylene and block copolymers of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane.

Another preferred class of nonionic surfactant can be described by the formula:

$$R_1O[CH_2CH(CH_3)O]_x[CH_2CH_2O]_y[CH_2CH(OH)R_2]$$

where R_1 represents a linear or branched chain aliphatic hydrocarbon group with 4-18 carbon atoms or mixtures thereof, R_2 represents a linear or branched chain aliphatic hydrocarbon rest with 2-26 carbon atoms or mixtures thereof, x is a value between 0.5 and 1.5, and y is a value of at least 15.

Another group of preferred non-ionic surfactants are the end-capped polyoxyalkylated non-ionics of formula:

$$R_1O[CH_2CH(R_3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR_2$$

where R_1 and R_2 represent linear or branched chain, saturated or unsaturated, aliphatic or aromatic hydrocarbon groups with 1-30 carbon atoms, R_3 represents a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl or 2-methyl-2-butyl group, x is a value between 1 and 30 and, k and j are values between 1 and 12, preferably between 1 and 5. When the value of x is >2 each R_3 in the formula above can be different. R_1 and R_2 are preferably linear or branched chain, saturated or unsaturated, aliphatic or aromatic hydrocarbon groups with 6-22 carbon atoms, where groups with 8 to 18 carbon atoms are particularly preferred. For the group R_3, H, methyl or ethyl is particularly preferred. Particularly preferred values for x are comprised between 1 and 20, preferably between 6 and 15.

As described above, in case x>2, each R_3 in the formula can be different. For instance, when x=3, the group R_3 could be chosen to build ethylene oxide (R_3=H) or propylene oxide (R_3= methyl) units which can be used in every single order for instance (PO)(EO)(EO), (EO)(PO)(EO), (EO)(EO)(PO), (EO)(EO)(EO), (PO)(EO)(PO), (PO)(PO)(EO) and (PO)(PO)(PO). The value 3 for x is only an example and bigger values

can be chosen whereby a higher number of variations of (EO) or (PO) units would arise. Particularly preferred end-capped polyoxyalkylated alcohols of the above formula are those where k=1 and j=1 originating molecules of simplified formula:

$R_1O[CH_2CH(R_3)O]_xCH_2CH(OH)CH_2OR_2$

Another group of preferred non-ionic surfactants are mixed alkoxylate fatty alcohol nonionic surfactants

The standard non-ionic surfactant structure is based on a fatty alcohol with a carbon C8 to C20 chain, wherein the fatty alcohol has been ethoxylated or propoxylated. The degree of ethoxylation is described by the number of ethylene oxide units (EO), and the degree of propoxylation is described by the number of propylene oxide units (PO). Such surfactants may also comprise butylene oxide units (BO) as a result of butoxylation of the fatty alcohol. Preferably, this will be a mix with PO and EO units. The surfactant chain can be terminated with a butyl (Bu) moiety.

Preferably the mixed alkoxylate fatty alcohol non-ionic surfactants comprise between 3 to 5 moles of the higher alkoxylate group and between 6 to 10 moles the higher lower group. Especially preferred are mixed alkoxylate fatty alcohol nonionic surfactants having 4 or 5 moles of the higher alkoxylate group and 7 or 8 moles of the lower alkoxylate group. According to one aspect of the invention a mixed alkoxylate fatty alcohol nonionic surfactant having 4 or 5 PO moles and 7 or 8 EO moles is especially preferred and good results have been obtained with for surfactants with 4 PO moles and 8 EO moles. In an especially preferred embodiment the mixed alkoxylate fatty alcohol nonionic surfactant is C12-15 8EO/4PO (commercially available as Genapol EP 2584 ex Clariant, Germany).

The use of mixtures of different non-ionic surfactants is suitable in the context of the present invention, for instance mixtures of alkoxylated alcohols and hydroxy group containing alkoxylated alcohols.

Other suitable surfactants are disclosed in WO 95/01416, which is incorporated herein by reference.

Preferably the non-ionic surfactants are present in the automatic dishwashing product in an amount of from 0.1 to 20 wt% by weight of the automatic dishwashing product, more preferably from 1 to 15 wt%, such as from 2 to 10 wt%.

Enzymes

The automatic dishwashing product may include one or more enzymes. It is preferred that the one or more enzymes are selected from proteases, lipases, amylases, cellulases and peroxidases, with proteases and amylases being most preferred. It is most preferred that protease and/or amylase enzymes are included in the products according to the invention as such enzymes are especially effective in dishwashing detergent compositions. Any suitable species of these enzymes may be used as desired. More than one species may be used.

Additional components

The skilled person will be aware of the kinds of ingredients that may be present in ADW (automatic dishwashing) products. The automatic dishwashing product of the present invention may comprise any other suitable ingredients known in the art.

For example, polymers intended to improve the cleaning performance of the automatic dishwashing product may also be included therein. For example sulphonated polymers may be used. Preferred examples include copolymers of $CH_2=CR^1CR^2R^3\text{-}O\text{-}C_4H_3R^4\text{-}SO_3X$ wherein R^1, R^2, R^3, R^4 are independently 1 to 6 carbon alkyl or hydrogen, and X is hydrogen or alkali with any suitable other monomer units including modified acrylic, fumaric, maleic, itaconic, aconitic, mesaconic, citraconic and methylenemalonic acid or their salts, maleic anhydride, acrylamide, alkylene, vinylmethyl ether, styrene and any mixtures thereof. Other suitable sulfonated monomers for incorporation in sulfonated (co)polymers are 2- acrylamido-2-methyl-1-propanesulphonic acid, 2-methacrylamido-2-methyl-1- propanesulphonic acid, 3-methacrylamido-2-hydroxy-propanesulphonic acid, allysulphonic acid, methallysulphonic acid, 2-hydroxy-3-(2 propenyloxy)propanesulphonic acid, 2-methyl-2-propenen-1-sulphonic acid, styrenesulphonic acid, vinylsulphonic acid, 3-sulphopropyl acrylate, 3-sulphopropylmethacrylate, sulphomethylacrylamide, sulphomethylmethacrylamide and water soluble salts thereof. Suitable sulphonated polymers are also described in US 5308532 and in WO 2005/090541, which are incorporated herein by reference.

When a sulfonated polymer is present, it is preferably present in an amount of at least 0.1 wt% by weight of the automatic dishwashing product, preferably at least 0.5 wt%, more preferably at least 1 wt%, and most preferably at least 3 wt%, up to 40 wt%,

preferably up to 25 wt%, more preferably up to 15 wt%, and most preferably up to 10 wt%.

The automatic dishwashing product may also comprise one or more foam control agents. Suitable foam control agents for this purpose are all those conventionally used in this field, such as, for example, silicones and their derivatives and paraffin oil. The foam control agents are preferably present in amounts of 0.5 wt% or less.

The automatic dishwashing product may also comprise minor, conventional, amounts of preservatives, fragrances, and the like.

Product format

The product may be in the form of a tablet, a powder, granules, a liquid, a gel, a paste, or combinations of two or more thereof.

The product may comprise a single composition or a plurality of compositions. For example, the product may comprise a single composition comprising the bleaching agent, the 5-methyl-*1H*-benzotriazole and, when present, the 4-methyl-*1H*-benzotriazole, the single composition preferably being in the form of a tablet, a powder, granules, a liquid, a gel or a paste.

In embodiments where the product comprises a plurality of compositions, the bleaching agent, the 5-methyl-*1H*-benzotriazole and, when present, the 4-methyl-*1H*-benzotriazole may each be provided in different compositions. Alternatively, the bleaching agent, the 5-methyl-*1H*-benzotriazole and, when present, the 4-methyl-*1H*-benzotriazole may be present in the same composition. Other permutations of components are possible. For example, the 5-methyl-*1H*-benzotriazole and, when present, the 4-methyl-*1H*-benzotriazole may be provided in the same composition, and the bleaching agent provided in a different composition. Alternatively, the 5-methyl-*1H*-benzotriazole and the bleaching agent may be provided in the same composition, and the 4-methyl-*1H*-benzotriazole, when present, being provided in a different composition.

Preferably, the product is in a unit dose or monodose form. In other words, the product comprises one or more compositions in the quantity required for a single wash cycle. The terms monodose and unit dose are used interchangeably throughout this disclosure.

The monodose product may comprise a tablet with a gel portion or layer. In these embodiments the bleaching agent, the 5-methyl-*1H*-benzotriazole and, when present, the 4-methyl-*1H*-benzotriazole may be provided in the tablet and/or the gel portion or layer. If compressed tablets form a portion of the automatic dishwashing product, they may be homogeneous or composed of multi-layers. If the tablets are multi-layered then different layers may comprise different parts of the detergent. This may be done to increase stability or increase performance, or both.

In an embodiment, the automatic dishwashing product is housed within a water soluble film or container, preferably a polyvinylalcohol film or container. The film or container may be a PVOH rigid capsule or film blister. The PVOH capsule or blister may have a single compartment or may be multi-compartment. Multi-compartment blisters or capsules may have different portions of the product in each compartment, or the same composition in each compartment. The distinct regions / compartments may contain any proportion of the total amount of ingredients as desired. The PVOH capsules or film blisters may be filled with tablets, powders, gels, pastes or liquids, or combinations of these, within the scope of the invention. These PVOH capsules or blisters may have a single compartment or may be multi-compartment. Multi-compartment blisters or capsules may have different portions of the product in each compartment, or the same composition in each compartment. Each compartment may contain any proportion of the total amount of ingredients as desired. Each compartment may comprise the 5-methyl-*1H*-benzotriazole, and/or the bleaching agent, and/or 4-methyl-*1H*-benzotriazole, and/or one or more builders, and/or one or more surfactants, and/or one or more enzymes. The PVOH capsules or film blisters may be filled with tablets, powders, granules, liquids, gels, pastes, or combinations of two or more thereof.

The film or container may be an injection moulded PVOH capsule with multiple compartments. Each compartment may comprise a different composition. Optionally, one or more of the compartments may contain a gel or liquid composition. Each compartment may comprise the 5-methyl-*1H*-benzotriazole, and/or the bleaching agent, and/or 4-methyl-*1H*-benzotriazole, and/or one or more builders, and/or one or more surfactants, and/or one or more enzymes. Each compartment may be filled with a tablet, a powder, granules, a liquid, a gel, a paste, or combinations of two or more thereof.

According to a second aspect, the present invention provides a method of automatic dishwashing, the method comprising supplying a product to an automatic dishwasher and releasing the product or a portion thereof into a wash cycle of the automatic

dishwasher, the product comprising an oxygen-releasing bleaching agent, 5-methyl-*1H*-benzotriazole and optionally 4-methyl-*1H*-benzotriazole,

wherein

when the product comprises 4-methyl-*1H*-benzotriazole, the 5-methyl-*1H*-benzotriazole and 4-methyl-*1H*-benzotriazole are present in a weight ratio of at least 4:1.

Preferably, the product is the product of the first aspect.

Preferably, the dishwasher contains silverware and/or copperware. The terms "silverware" and "copperware" as used herein refer to articles formed of or coated with silver and copper respectively. It is to be understood that the terms silver and copper encompass the elements themselves and alloys containing the elements. As explained above, the corrosion inhibitor of the present invention is effective in inhibiting the corrosion of copper and silver. It is to be understood that the silverware and/or copperware are present in the dishwasher during the wash cycle of the method.

Preferably, the product is formulated to provide, in use, a cleaning solution having a pH of less than 11.5 at a wash cycle temperature of from 40 to 60 °C, more preferably from 7 to 10.5. That is, the step of releasing the product into the dishwasher preferably comprises dissolving and/or dispersing the product or a portion thereof in water at a temperature of from 40 to 60 °C to form a cleaning solution having a pH of less than 11.5, or from 7 to 10.5, and contacting soiled articles (such as silverware and copperware) with the cleaning solution. In other words, the product is preferably a "low-alkaline" formulation, as discussed above.

In the step of releasing the product or a portion thereof into a wash cycle of the automatic dishwasher, from 0.1 to 6.5 grams of bleaching agent and/or from 1 to 500 milligrams of 5-methyl-*1H*-benzotriazole are preferably released into the wash cycle, more preferably from 1 to 4 grams of bleaching agent and from 10 to 400 milligrams of 5-methyl-*1H*-benzotriazole.

According to a third aspect, the present invention provides a use of 5-methyl-*1H*-benzotriazole, substantially in the absence of 4-methyl-*1H*-benzotriazole for reducing corrosion of silver and/or copper by a bleaching agent in an automatic dishwashing process.

By “substantially in the absence of” is meant in a product comprising less than 0.02 wt% 4-methyl-*1H*-benzotriazole. Preferably, the use is essentially in the absence of or in the absence of or in the absence of 4-methyl-*1H*-benzotriazole.

Preferably, the bleaching agent is an oxygen-releasing bleaching agent.

Preferably, the use of the third aspect comprises the use of the product of the first aspect, optionally in the process of the second aspect.

All percentages used in this disclosure are by weight unless otherwise specified.

The present invention will now be described in relation to the following non-limiting example.

Example

In order to evaluate the feasibility of 5-methyl-*1H*-benzotriazole for use in automatic dishwashing detergents, a base powder formulation (**1**) without any silver/copper corrosion inhibitors was prepared and tested. To 20 g of this formulation were added either 27 mg of a TTA powder (**2**) or 16 mg of 5-methyl-*1H*-benzotriazole powder (**3**). The TTA powder was a commercially available 60:40 mixture of 5-methyl-*1H*-benzotriazole and 4-methyl-*1H*-benzotriazole.

The composition of formulation (**1**) was as follows:

Raw Material	**g/dose**
Sodium Percarbonate	2.35
TAED	0.60
Mn-TACN Catalyst	0.015
Builders	7.54
Surfactants/polymers	1.66
Sodium Carbonate/bicarbonate	7.52
Enzymes	0.11
Antifoam	0.20
TOTAL	**20.00**

Dishwasher Machine: G 1223 SC GSL2
Program: P6: 65°C – 10 min /65°C
Water hardness: 21 °dH or <1 °dH
Rinse Aid: without rinse aid
Evaluators: 2 trained people

The averaged results are shown in the following Table.

Test product		**1 Non-inventive Mixture** 20g base powder			**2 Non-inventive Mixture** 20g base powder + 0.027g TTA	**3 Inventive Mixture** 20g base powder + 0.016g 5-Methyl-*1H*-benzotriazole
Silver tarnishing	**21°dH water**	25	cycles	**1.0**	**3.1**	**3.0**
		0	cycles	5.0	5.0	5.0
	< 1°dH water	25	cycles	**2.2**	**3.6**	**3.9**
		0	cycles	5.0	5.0	5.0

Key:

5 = no discolouration/shine loss
4 = minor discolouration/shine loss
3 = discolouration/shine loss visible
2 = strong discolouration/shine loss
1 = very strong discolouration/shine loss

No significant differences were found between the two silver/copper protecting agents after 25 wash cycles. Both were effective in inhibiting silver tarnishing. These results were confirmed at two different water hardnesses.

The foregoing detailed description has been provided by way of explanation and illustration, and is not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments illustrated herein will be apparent to one of ordinary skill in the art, and remain within the scope of the appended claims and their equivalents.

Claims:

1. An automatic dishwashing product comprising a bleaching agent, 5-methyl-*1H*-benzotriazole and optionally 4-methyl-*1H*-benzotriazole,

wherein when the product comprises 4-methyl-*1H*-benzotriazole, the 5-methyl-*1H*-benzotriazole and the 4-methyl-*1H*-benzotriazole are present in a weight ratio of at least 4:1.

2. An automatic dishwashing product according to claim 1, wherein when the product comprises 4-methyl-*1H*-benzotriazole, the 5-methyl-*1H*-benzotriazole and the 4-methyl-*1H*-benzotriazole are present in a weight ratio of at least 10:1.

3. An automatic dishwashing product according to claim 1 or claim 2, wherein the 5-methyl-*1H*-benzotriazole is present in an amount of 0.001 to 1 wt% by weight of the product.

4. An automatic dishwashing product according to any of the preceding claims, wherein the product does not comprise 4-methyl-*1H*-benzotriazole.

5. An automatic dishwashing product according to any of the preceding claims, wherein the bleaching agent and the 5-methyl-*1H*-benzotriazole are present in a weight ratio of from 20:1 to 200:1.

6. An automatic dishwashing product according to any of the preceding claims, wherein the bleaching agent is an oxygen-releasing bleaching agent.

7. An automatic dishwashing product according to any of the preceding claims, wherein the product has a pH of less than 11.5 at 1 wt% aqueous solution at 20 °C.

8. An automatic dishwashing product according to any of the preceding claims, the automatic dishwashing product further comprising:

one or more builders, and/or

one or more surfactants, and/or

one or more enzymes.

9. An automatic dishwashing product according to any of the preceding claims, wherein the product is:

in a unit dose form; and/or

housed within a water soluble or water dispersible film or container, preferably a polyvinyl alcohol film or container.

10. A method of automatic dishwashing, the method comprising supplying a product to an automatic dishwasher and releasing the product or a portion thereof into a wash cycle of the automatic dishwasher, the product comprising a bleaching agent, 5-methyl-*1H*-benzotriazole and optionally 4-methyl-*1H*-benzotriazole,

wherein

when the product comprises 4-methyl-*1H*-benzotriazole, the 5-methyl-*1H*-benzotriazole and 4-methyl-*1H*-benzotriazole are present in a weight ratio of at least 4:1.

11. A method according to claim 10, wherein the automatic dishwasher contains silverware and/or copperware.

12. A method according to claim 10 or claim 11, wherein the product is formulated to provide, in use, a cleaning solution having a pH of less than 11 at a wash cycle temperature of from 40 to 60 °C.

13. A method according to any of claims 10 to 12, wherein in the step of releasing the product or a portion thereof into a wash cycle of the automatic dishwasher, from 0.1 to 6.5 grams of bleaching agent and/or from 1 to 500 milligrams of 5-methyl-*1H*-benzotriazole are released into the wash cycle.

14. Use of 5-methyl-*1H*-benzotriazole, substantially in the absence of 4-methyl-*1H*-benzotriazole, for reducing corrosion of silver and/or copper by a bleaching agent in an automatic dishwashing process.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/073126

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/28 C11D3/39 C11D3/48 C11D17/00 C11D17/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/025740 A1 (RECKITT BENCKISER NV [NL]; CABIROL MARINE [DE] ET AL.) 1 March 2012 (2012-03-01) claims 7,14 claims 7,15 page 1, lines 6-8; claim 12 page 13, lines 22-23 page 5, lines 9-10 the whole document -----	1-14
X	GB 1 347 008 A (CIBA GEIGY UK LTD) 13 February 1974 (1974-02-13) example 1; table I example 10; table I; compound 0.5: third column (0.8) page 2, lines 75-82 the whole document -----	1-14

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 November 2019	02/12/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Yildirim, Zeynep

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/073126

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 194 368 B1 (WAESCHENBACH GUIDO [DE] ET AL) 27 February 2001 (2001-02-27) claim 3 column 4, lines 4-5 column 7, lines 61-62 the whole document -----	1-14

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/073126

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012025740 A1	01-03-2012	AU 2011294884 A1	07-03-2013
		BR 112013004567 A2	06-09-2016
		CA 2809551 A1	01-03-2012
		CN 103180426 A	26-06-2013
		EP 2609188 A1	03-07-2013
		JP 2013538268 A	10-10-2013
		RU 2013113564 A	10-04-2015
		US 2013199569 A1	08-08-2013
		WO 2012025740 A1	01-03-2012
		ZA 201301317 B	30-04-2014
GB 1347008 A	13-02-1974	AR 193227 A1	11-04-1973
		AU 456155 B2	12-12-1974
		BE 775231 A	12-05-1972
		CA 964447 A	18-03-1975
		CH 561290 A5	30-04-1975
		DE 2155767 A1	25-05-1972
		ES 396933 A1	01-03-1975
		FR 2114466 A5	30-06-1972
		GB 1347008 A	13-02-1974
		IT 944863 B	20-04-1973
		NL 7115604 A	16-05-1972
		SE 368036 B	17-06-1974
		ZA 7107522 B	30-08-1972
US 6194368 B1	27-02-2001	AT 198349 T	15-01-2001
		AU 6413096 A	10-02-1997
		CA 2226143 A1	30-01-1997
		EP 0842257 A1	20-05-1998
		ES 2155613 T3	16-05-2001
		US 6194368 B1	27-02-2001
		WO 9703177 A1	30-01-1997