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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 May 2007 (10.05.2007)

PCT

(10) International Publication Number
WO 2007/052064 A1

(51) International Patent Classification:
C11D 3/00 (2006.01) *C11D 3/20* (2006.01)
C11D 3/33 (2006.01) *C11D 3/37* (2006.01)

(21) International Application Number:
PCT/GB2006/004149

(22) International Filing Date:
7 November 2006 (07.11.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0522658.4 7 November 2005 (07.11.2005) GB

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2007/052064 A1

(54) Title: COMPOSITION

(57) Abstract: A dishwasher detergent composition, preferably pH neutral, and comprising a strong biodegradable builder and optionally a bleach, and optionally a sulfonated polymer .

COMPOSITION

The invention relates to a detergent composition for machine dishwashing.

In recent years there has been an ever increasing trend towards safer and environmentally friendly detergent compositions. This has led to development of alternative complexing agents (builders), which are used instead of predominantly phosphorous based builders. Phosphate builders can be connected with eutrophication issues.

On the other hand phosphates can bind calcium and magnesium ions, can act as alkalinity source for the detergent, they are used to buffer the wash liquor in a dishwasher above pH 9 together with other chemicals such as disilicate, metasilicates and soda.

Phosphates are also able to disperse existing calcium carbonate in the wash liquor to prevent spotting on glasses.

Thus, replacing phosphates in a detergent means to compensate at least four different functions in an alkaline detergent. (1) providing alkalinity; (2) buffering capacity, (3)complexing of magnesium and calcium ions; and (4) dispersing capacity of calcium carbonate

The use of more environmentally friendly biodegradable complexing agents, such as β-alaninediacetic acid (β-ADA) and isoserinediacetic acid (ISDA) in detergents is disclosed in DE-A-3,829,847 and DE-A-4,036,995.

However, these compounds have low complexing action and only a poor replacement for the conventional builders in the finished composition.

Other documents disclosing the use of biodegradable builders in detergent compositions include EP-A-550,087 which discloses a biodegradable oxydissucinate builder in detergent compositions and WO 97/23450 which discloses biodegradable cysteic monosuccinic acid builder in detergent compositions. JP2000063894 and JP2001003089 disclose glutamic diacetic acid builder in detergent compositions. US 4132735 discloses detergent compositions comprising biodegradable acrylate polymer builders.

One other environmentally friendly builder that has been used in dishwasher detergent formulations are salts of citric acid. This has the advantage that these salts are biodegradable, and environmentally friendly. However, the builder performance of citric acid salts is far inferior to that of phosphorus based builders. Additionally this poor performance is even further compromised with increasing temperature: salts of citric acid display especially poor activity above 45°C.

Indeed the dishwasher detergents proposed to date which use environmentally friendly complexing agents have the disadvantage that they are only effective at a relatively high pH. In order to provide this high pH, pH adjusting agents usually need to be added to the composition. These pH adjusting agents can act as additional buffering system, but cause side problems of filming and spotting on dishes. Repeated wash cycles can also lead to glass and machine corrosion, and lime-scale build-up, even on dishes.

It is an object of the invention to obviate /mitigate the issues outlined above and/or to offer detergent compositions with usage and/or environmental benefits.

According to the present invention there is provided a dishwasher detergent composition comprising a strong biodegradable builder.

Preferred embodiments of the invention produce pH-neutral washing liquors. For the purposes of this specification pH-neutral is defined as pH 5 to pH 8, more preferably from pH 5.5 to pH 7.8 and most preferably from pH 6 to pH 7.7, especially pH 7 to 7.6; when dissolved 1:100 (wt:wt, composition:water) in de-ionised water at 20°C, measured using a conventional pH meter.

Other embodiments of the invention produce alkaline washing liquors. For the purposes of this specification alkaline is defined as pH greater than 8. A preferred pH range is pH 8.5 to pH 11; when dissolved 1:100 (wt:wt, composition:water) in de-ionised water at 20°C, measured using a conventional pH meter.

Surprisingly, it has been found that compositions according to the invention have excellent properties. In particular the detergents have been found to effectively remove food residues combined with the ability to prevent or even to remove the build-up of precipitates formed by Ca- and Mg-ions; such as limescale.

Further, compositions of the invention have been found to be particularly good in preventing scale deposition and/or in rinse properties.

Further, certain compositions of the invention have been found to have an advantage over comparator compositions

not of the invention, in terms of their ability to be press-formed into solid bodies such as tablets.

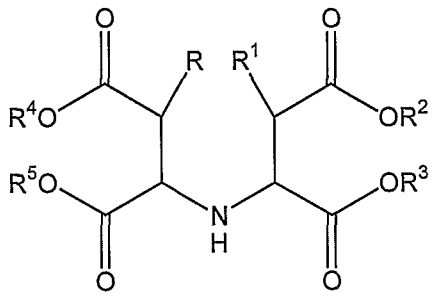
Preferably the composition has a solids content of more than 25%, preferably more than 50%.

The composition may, for example, be in the form of a tablet, rod, ball or lozenge. The composition may be a particulate form, loose or pressed to shape or may be formed by injection moulding or by casting or by extrusion. The composition may be encased in a water soluble wrapping, for, example of PVOH or a cellulosic material. The composition may be a gel.

Preferably the strong biodegradable builder is present in the composition in an amount of at least 0.1 wt%, preferably at least 0.5 wt%, more preferably at least 1 wt%, and most preferably at least 4 wt%.

Preferably the strong biodegradable builder is present in the composition in an amount of up to 65wt%, preferably up to 50wt%, more preferably up to 30wt%, and most preferably up to 15 wt%.

Most preferably the strong biodegradable builder is an amino acid based compound or a succinate based compound. Preferred examples of amino acid based compounds include MGDA (methyl-glycine-diacetic acid, and salts thereof) and glutamic-N,N-diacetic acid. Preferred succinate compounds are described in US-A-5,977,053 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, denoting hydrogen, alkyl radicals having 1 to 12 C atoms or hydroxyl-substituted alkyl radicals having 2 to 3 C atoms. A preferred example is tetrasodium imminosuccinate.

Compositions of the invention containing MGDA have been found to be particularly well suited to being press-formed into solid bodies such as tablets.

Preferably a secondary builder (or cobuilder) is present in the composition. 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.

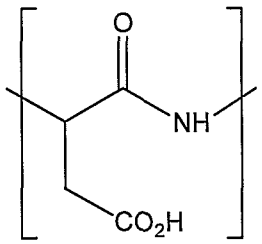
Suitable polycarboxylic acids are acyclic, alicyclic, heterocyclic and aromatic carboxylic acids, in which case they contain at least two carboxyl groups which are in each case separated from one another by, preferably, no more than two carbon atoms.

Polycarboxylates which comprise two carboxyl groups include, for example, water-soluble salts of succinic acid, malonic acid, (ethylenedioxy)diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid. Polycarboxylates which contain three carboxyl groups include, for example, water-soluble citrate. Correspondingly, a suitable hydroxycarboxylic acid is, for example, citric acid.

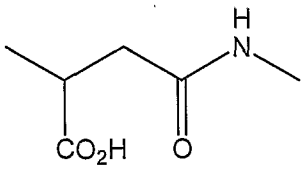
Another specific secondary builder for dishwasher detergents which can be mentioned is a polymer, derived from aspartic acid

$$HOOC\text{-}CH(NH_2)\text{-}CH_2\text{-}COOH$$

containing monomer units of the formula



and



Another suitable polycarboxylic acid is the homopolymer of acrylic acid.

Other suitable builders are disclosed in WO 95/01416, to the contents of which express reference is hereby made.

Particular preference is given to a builder system of the salt of a hydroxycarboxylic acid or of the mixture of a

hydroxycarboxylic acid and the salt of a hydroxycarboxylic acid. Both the hydroxycarboxylic acid and the salt of the hydroxycarboxylic acid could be replaced completely or partially by tripolyphosphate.

However, although phosphorus-containing secondary builders may be present in this invention preferred compositions have no phosphorus-containing compound(s).

The builder system preferably consists of a hydroxypolycarboxylic acid containing 2-4 carboxyl groups (or acidic inorganic salts), which can be mixed with its salt to adjust the pH. Citric acid or a mixture of sodium citrate with citric acid is preferably used. For adjustment of the pH, which may be required to provide a composition within the range defined in this invention, mixtures having a major proportion of citric acid, for example, are suitable, depending on the other constituents of the mixture.

Sulfonated polymers are suitable for use in the present invention. Preferred examples include copolymers of $CH_2=CR^1-CR^2R^3-O-C_4H_3R^4-SO_3X$ 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-propanesulfonic acid, 2-methacrylamido-2-methyl-1-propanesulfonic acid, 3-methacrylamido-2-hydroxy-propanesulfonic acid, allysulfonic acid, methallysulfonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propenen-1-sulfonic acid, styrenesulfonic acid,

vinylsulfonic acid, 3-sulfopropyl acrylate, 3-sulfopropylmethacrylate, sulfomethylacrylamide, sulfomethylmethacrylamide and water soluble salts thereof.

Suitable sulfonated polymers are also described in US 5308532 and in WO 2005/090541.

When a sulfonated polymer is present, it is preferably present in the composition in an amount of at least 0.1 wt%, preferably at least 0.5 wt%, more preferably at least 1 wt%, and most preferably at least 3 wt%.

When a sulfonated polymer is present, it is preferably present in the composition in an amount of up to 40wt%, preferably up to 25wt%, more preferably up to 15wt%, and most preferably up to 10 wt%.

Sulfonated polymers are used in detergency applications as polymers to disperse Ca-phosphate compounds and prevent their deposition. To our surprise we have found them to give cleaning benefits in combination even with preferred phosphorus-free compositions of the present invention.

A bleach may be present in a composition of the invention.

When a bleach is present, it is preferably present in the composition in an amount of at least 1 wt%, more preferably at least 2 wt%, more preferably at least 4 wt%.

When a bleach is present, it is preferably present in the composition in an amount of up to 30wt%, more preferably up to 20wt%, and most preferably up to 15wt%.

Most preferably a bleach is selected from inorganic perhydrates or organic peracids and the salts thereof.

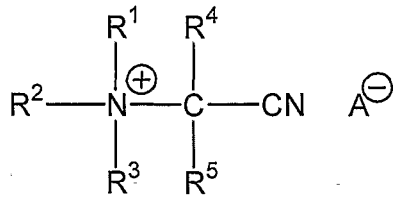
Examples of inorganic perhydrates are persulfates such as peroxymonopersulfate (KMPS). Perborates or percarbonates are not excluded but are less favoured. The inorganic perhydrates are normally alkali metal salts, such as lithium, sodium or potassium salts, in particular sodium salts. The inorganic perhydrates may be present in the detergent as crystalline solids without further protection. For certain perhydrates, it is however advantageous to use them as granular compositions provided with a coating which gives the granular products a longer shelf life.

A percarbonate may be present but is less preferred. When one is present the preferred percarbonate is sodium percarbonate of the formula $2Na_2CO_3.3H_2O_2$. A percarbonate, when present, is preferably used in a coated form, to increase its stability.

Organic peracids include all organic peracids traditionally used as bleaches, including, for example, perbenzoic acid and peroxycarboxylic acids such as mono- or diperoxyphthalic acid, 2-octyldiperoxysuccinic acid, diperoxydodecanedicarboxylic acid, diperoxy-azelaic acid and imidoperoxycarboxylic acid and, optionally, the salts thereof. Especially preferred is phthalimidoperhexanoic acid (PAP).

The dishwasher detergent according to the invention and containing a bleach can also comprise one or more bleach activators. These are preferably used in detergents for dishwashing cycles at temperatures in the range below 60°C in order to achieve an adequate bleaching action. Particularly suitable examples are N- and O-acyl

compounds, such as acylated amines, acylated glycolurils or acylated sugar compounds. Preference is given to pentaacetylglucose (PAG) and tetraacetylglycoluril (TAGU). Also favoured are ammonium nitrile compounds of formula 1 below:



in which R^1, R^2, and R^3 are the same of different and can be linear or branched C1-24 alkyl, C2-24 alkenyl, or c2-4-C1-4 alkyl groups, or substituted or unsubstituted benzyl; or wherein R^1 and R^2 together with the nitrogen atom from a ring structure. Other suitable bleach activators are, however, catalytically active metal complexes and, preferably, transition metal complexes. Other suitable bleach activators are disclosed in WO 95/01416 (various chemical classes) and in EP-A-1 209 221 (cyclic sugar ketones).

Usually the detergent composition comprises other conventional dishwasher detergent components.

For example the composition may contain surface active agents such as an anionic, non-ionic, cationic, amphoteric or zwitterionic surface active agents or mixtures thereof. Many such 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.

One possible class of nonionic surfactants are ethoxylated non-ionic surfactants prepared by the reaction of a monohydroxy alkanol or alkylphenol with 6 to 20 carbon atoms with preferably at least 12 moles particularly preferred at least 16 moles, and still more preferred at least 20 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 preferred embodiment of the invention, the non-ionic surfactants additionally comprise propylene oxide units in the molecule. Preferably this PO units constitute up to 25% by weight, preferably up to 20% by weight and still more preferably up to 15% by weight of the overall molecular weight of the non-ionic surfactant. Particularly preferred surfactants are ethoxylated mono-hydroxy alkanols or alkylphenols, which additionally comprises polyoxyethylene-polyoxypropylene block copolymer units. The alcohol or alkylphenol portion of such surfactants constitutes more than 30%, preferably more than 50%, more preferably more than 70% 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 nonionic 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, alyphatic 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, alyphatic or aromatic hydrocarbon groups with 6-22 carbon atoms, where group with 8 to 18 carbon atoms are particularly preferred. For the group R^3 H, methyl or ethyl are 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:

$$R^1O[CH_2CH(R^3)O]_xCH_2CH(OH)CH_2OR^2$$

The use of mixtures of different nonionic surfactants is suitable in the context of the present invention for instances mixtures of alkoxylated alcohols and hydroxy group containing alkoxylated alcohols.

Other suitable surfactants are disclosed in WO 95/01416, to the contents of which express reference is hereby made.

The dishwasher detergent according to the invention can also comprise one or more foam control agents. Suitable foam control agents for this purpose are all those used

in this field, such as, for example, silicones and paraffin oil.

The foam control agents are preferably present in the dishwasher detergent according to the invention in amounts of less than 5% by weight of the total weight of the detergent.

The dishwasher detergent according to the invention can also comprise a source of acidity or a source of alkalinity, to obtain the desired pH, on dissolution. A source of acidity may suitably be any of the components mentioned above, which are acidic; for example polycarboxylic acids. A source of alkalinity may suitably be any of the components mentioned above, which are basic; for example any salt of a strong base and a weak acid. However additional acids or bases may be present. In the case of alkaline compositions silicates may be suitable additives. Preferred silicates are sodium silicates such as sodium disilicate, sodium metasilicate and crystalline phyllosilicates.

The dishwasher detergent according to the invention can also comprise a silver/copper corrosion inhibitor. This term encompasses agents which are intended to prevent or reduce the tarnishing of non-ferrous metals, in particular of silver and copper. Preferred silver/copper corrosion inhibitors are benzotriazole or bis-benzotriazole and substituted derivatives thereof.

Other suitable agents are organic and/or inorganic redox-active substances and paraffin oil.

Benzotriazole derivatives are those compounds in which the available substitution sites on the aromatic ring are partially or completely substituted. Suitable

substituents are linear or branch-chain C_{1-20}-alkyl groups and hydroxyl, thio, phenyl or halogen such as fluorine, chlorine, bromine and iodine. A preferred substituted benzotriazole is tolyltriazole.

Suitable bis-benzotriazoles are those in which the benzotriazole groups are each linked in the 6-position by a group X, where X may be a bond, a straight-chain alkylene group which is optionally substituted by one or more C_{1-4}-alkyl groups and preferably has 1-6 carbon atoms, a cycloalkyl radical having at least 5 carbon atoms, a carbonyl group, a sulfuryl group, an oxygen atom or a sulfur atom. The aromatic rings of the bis-benzotriazoles may be substituted as defined above for benzotriazole.

Suitable organic redox-active substances are, for example, ascorbic acid, indole, methionine, an N-mono-(C_1-C_4-alkyl)glycine, an N,N-di-(C_1-C_4-alkyl)glycine, 2-phenylglycine or a coupler and/or developer compound chosen from the group consisting of diaminopyridines, aminohydroxypyridines, dihydroxypyridines, heterocyclic hydrazones, aminohydroxypyrimidines, dihydroxypyrimidines, tetraaminopyrimidines, triaminohydroxypyrimidines, diaminodihydroxypyrimidines, dihydroxynaphthalenes, naphthols, pyrazolones, hydroxyquinolines, aminoquinolines, of primary aromatic amines which, in the ortho-, meta- or paraposition, have another hydroxyl or amino group which is free or substituted by C_1-C_4-alkyl or C_2-C_4-hydroxyalkyl groups, and of di- or trihydroxybenzenes.

Suitable inorganic redox-active substances are, for example, metal salts and/or metal complexes chosen from the group consisting of manganese, titanium, zirconium, hafnium, vanadium, cobalt and cerium salts and/or

complexes, the metals being in one of the oxidation states II, III, IV, V or VI.

Particularly suitable metal salts and/or metal complexes are chosen from the group consisting of $MnSO_4$, Mn(II) citrate, Mn(II) stearate, Mn(II) acetylacetonate, Mn(II) [1-hydroxyethane-1,1-diphosphonate], V_2O_5, V_2O_4, VO_2, $TiOSO_4$, K_2TiF_6, K_2ZrF_6, $CoSO_4$, $Co(NO_3)_2$ and $Ce(NO_3)_3$.

Organic and inorganic redox-active substances which are suitable as silver/copper corrosion inhibitors are also mentioned in WO 94/26860 and WO 94/26859, to the contents of which reference is hereby made.

Suitable paraffin oils are predominantly branched aliphatic hydrocarbons having a number of carbon atoms in the range from 20 to 50. Preference is given to the paraffin oil chosen from predominantly branched-chain C_{25-45} species having a ratio of cyclic to noncyclic hydrocarbons of from 1:10 to 2:1, preferably from 1:5 to 1:1.

If a silver/copper corrosion inhibitor is present in the dishwasher detergent according to the invention, it is preferably present in an amount of from 0.01 to 5% by weight, particularly preferably in an amount of from 0.1 to 2% by weight, of the total weight.

Other customary additives are, for example, dyes and perfumes and optionally in the case of liquid products, preservatives, suitable examples of which are compounds based on isothiazolinone.

The composition preferably comprises one or more enzymes, preferably selected from protease, lipase, amylase, cellulase and peroxidase enzymes. Such enzymes are

commercially available and sold, for example, under the registered trade marks Esperase, Alcalase and Savinase by Nova Industries A/S and Maxatase by International Biosynthetics, Inc. Desirably the enzyme(s) is/are present in the composition in an amount of from 0.01 to 3wt%, especially 0.01 to 2wt% (active enzyme(s) present).

The composition is described with reference to the following non-limiting Examples.

Examples

Dispersing Capacity of complexing agents

Method: Determination of calcium carbonate dispersing capacity

1. Dissolve 1 g product (= builder) in 100ml deionized water.
2. Neutralize, if necessary, with 1M NaOH.
3. Add 10 ml of a 10% Na2CO3 solution
4. Adjust pH to 10 with NaOH or HCl as required.
5. Keep pH and temperature constant during titration.
6. Titrate with 0.25M calcium acetate solution until the solution becomes turbid.

This method is in accordance with the scientific paper by F. Richter and E.W. Winkler, published in Tenside Detergent, 1987, 4, pp.213-216.

Builder	$CaCO_3$ dispersing capacity in mg/g builder at 25°C		Buffering capacity
STPP (Benchmark)	252	240	YES
MGDA	344	259	NO
Dissolvine	250	234	NO

IDS	227	130	NO
Trisodium citrate	158	31	NO

MGDA: (Methyl Glycine-N,N-diacetic acid), sodium salt, Trilon M™ from BASF.
Dissolvine™: (N,N-diacetic-glutamic acid) , sodium salt, from Akzo Nobel.
IDS: Imino-disuccinate, sodium salt, Baypure CX 100™ from Lanxess.

All dispersing values were measured at pH 10.

It can be seen from the results that MGDA and Dissolvine are as good as or better than the phosphate regarding the dispersing capacity at room temperature and at 50°C (dishwash cycle temperature).

IDS is a little less effective at pH 10.

Citrate cannot compensate for STPP at all, because it cannot disperse calcium carbonate at 50°C.

Overall, this measurement gives an indication that citrate alone cannot replace STPP, but can act as a base material for a dishwasher detergent formulation.

Citrate needs to be combined with a material that shows less temperature sensitive behaviour such as Dissolvine, MGDA or IDS.
The missing buffering capacity can be compensated for by formulating a base of citrate and its acid form.

Formulation Examples

A base formulation (powder) was prepared as below.

Component	Wt%
Strong Biodegradable Builder	5.0
Sodium Citrate	69.8
Citric acid	2.0
PAP bleach	7.0
Amylase*[1]	0.4
Protease*[2]	1.1
Sulfonated polymer*[3]	5.0
PEG 6000	2.0
PEG 1500	7.0
Surfactant*[4]	0.5
BTA	0.1
Perfume	0.1

*[1] Duramyl™

*[2] Properase™

*[3] Sulfonated polyacrylic acid copolymer Acusol 587™. Acusol 588™ or Alcoguard 4080™ may be substituted.

*[4] C16-18 fatty alcohol 3EO-3PO

For formulation 1 the builder was MGDA, supplied as Trilon M™ from BASF.

For formulation 2 the builder was (N,N-diacetic-glutamic acid), supplied as Dissolvine™ from Akzo Nobel.

For formulation 3 the builder was Imino-disuccinate, supplied as Baypure CX 100™ from Lanxess.

Formulation 4 has only sodium citrate 75% as builder.

The formulations all had a pH of 7.5. Minor amounts of the citric acid were added or subtracted from the 2wt% value in order to achieve the pH value.

Application Examples

The builder capability (and other cleaning capabilities) was tested in a Miele 651 dishwashing machine using a 50°C cycle Normal, according to the method IKW. In each case 20g of the powder was added to the dosing chamber of the dishwasher. The water hardness was 21°gH. The results (given in Table 1) are expressed on a scale of 1-10 (1 being worst and 10 being best).

Table 1

Stain	**Formulation 1**	**Formulation 2**	**Formulation 3**	**Formulation 4**
Bleachable (Tea)	7.5	7.6	7.0	5.9
Starch - dried on oat flakes	8.0	7.8	7.5	7.5
Starch - dried on starch mix	9.3	9.6	9.8	9.4
Protein - dried on minced meat	6.7	6.5	5.7	6.7
Burnt-on (milk)	5.9	6.1	5.9	5.8
	Av. 7.4	Av. 7.5	Av. 7.1	Av. 7.0

These results show that the strong biodegradable builders provide excellent cleaning results even at pH 7.5.

To increase the performance of the bleach and the protease, the concentration of those components can be increased.

In detail, we find much better results on tea stains, with the formulations of the invention compared with the know formulation, formulation 4. This is probably due to better $CaCO_3$-dispersing properties of strong organic builders compared with the pure citrate formulation 4. In other tests the results were generally good, for all four formulations.

Claims

1. A dishwasher detergent composition comprising a strong biodegradable builder.

2. A composition as claimed in claim 1, comprising also a sulfonated polymer.

3. A composition as claimed in claim 2, wherein the sulfonated polymer is a polymer or copolymer which includes, as a or the monomer unit, a compound of formula

$$CH_2=CR^1-CR^2R^3-O-C_4H_3R^4-SO_3X$$

wherein R^1, R^2, R^3, R^4 are independently 1 to 6 carbon alkyl or hydrogen, and X is hydrogen or alkali.

4. A composition as claimed in claim 2 or 3, wherein the sulfonated polymer, includes, as a or the monomer unit,
2-acrylamido-2-methyl-1-propanesulfonic acid.

5. A composition as claimed in claim 2, 3 or 4, wherein the sulfonated polymer is present in an amount of from 0.5 wt% up to 40 wt%.

6. A composition as claimed in any preceding claim, wherein the composition yields a pH-neutral liquid washing medium.

7. A composition as claimed in any of claims 1 to 5 in which the composition yields an alkaline liquid washing medium.

8. A composition as claimed in any preceding claim, wherein the strong biodegradable builder is present in the composition in an amount of from 0.1 wt% to 65wt%.

9. A composition as claimed in any preceding claim, wherein the strong biodegradable builder is an amino acid based compound or a succinic acid based compound.

10. A composition as claimed in claim 9, wherein the amino acid based compound is selected from methyl-glycine-diacetic acid, and salts thereof and glutamic-N,N-diacetic acid and salts thereof.

11. A composition as claimed in any preceding claim, wherein the composition comprises a secondary builder selected from homopolymers and copolymers of polycarboxylic acids and their partially or completely neutralized salts, monomeric polycarboxylic acids and hydroxycarboxylic acids and their salts, and from phosphates and phosphonates; including mixtures of any such substances.

12. A composition as claimed in claim 11, wherein the secondary builder is organic.

13. A composition as claimed in claim 11, wherein the composition comprises polyhydroxycarboxylic acid containing 2-4 carboxyl groups or a salt thereof; preferably with no inorganic secondary builder.

14. A composition as claimed in any preceding claim, comprising from 1 wt% to 30 wt% of a bleach selected from a peroxymonopersulfate and from an organic peracid or salt derived therefrom.

15. A composition as claimed in any preceding claim, comprising 0.01 to 3wt% of one or more enzymes,

preferably selected from protease, lipase, amylase, cellulase and peroxidase enzymes.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/004149

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/00 C11D3/33 C11D3/20 C11D3/37

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 practical, 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 98/13467 A (UNILEVER NV [NL]; UNILEVER PLC [GB]) 2 April 1998 (1998-04-02) claims examples page 3, line 12 - line 16 page 7, line 23 - page 9, line 2 page 11, line 13 - line 24	1,6-13, 15
X	US 6 194 373 B1 (SAITO MAKOTO [JP] ET AL) 27 February 2001 (2001-02-27) claims examples column 1, line 65 - column 2, line 3 column 3, line 40 - column 4, line 43 column 5, line 7 - line 18 column 5, line 64 - line 67	1,7-10

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[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
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 January 2007	05/02/2007

Name and mailing address of the ISA	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2001 003089 A (TEEPOL LTD) 9 January 2001 (2001-01-09) cited in the application the whole document	1,6-10
X	DE 38 29 847 A1 (BASF AG [DE]) 15 March 1990 (1990-03-15) cited in the application claims examples page 2, line 20 - line 22 page 4, line 27 - line 31	1,6-9, 11-15
X	EP 0 550 087 A (UNILEVER NV [NL]; UNILEVER PLC [GB]) 7 July 1993 (1993-07-07) cited in the application the whole document	1,6-9, 11-14
X	US 4 132 735 A (LAMBERTI VINCENT ET AL) 2 January 1979 (1979-01-02) cited in the application claim examples column 4, line 14 - line 53	1,6-8, 11-15
X	WO 2005/090541 A (PROCTER & GAMBLE [US]; NAT STARCH ALCO CHEMICAL [US]; WAITS LESLIE DAW) 29 September 2005 (2005-09-29) cited in the application claims 1,4-9,16-18 table X examples 14,19,33-36,41-43 page 11, last paragraph - page 12, paragraph 1	1-15
X	WO 00/58228 A (CALGON CORP [US]) 5 October 2000 (2000-10-05) claims 1,6,10-15 examples page 11, line 12 - line 28	1-6,8
X	US 5 968 884 A (GOPALKRISHNAN SRIDHAR [US] ET AL) 19 October 1999 (1999-10-19) claims 1,- column 8, line 42 - line 58 column 4, line 65 - column 5, line 5	1,2,5, 7-14
X	US 3 875 070 A (VON PRAUN FERDINAND ET AL) 1 April 1975 (1975-04-01) claims examples column 1, line 28 - line 30	1,2,5-8, 11,14

-/--

2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/004149

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 509 382 A2 (GRACE W R & CO [US] HAMPSHIRE CHEMICAL CORP [US]) 21 October 1992 (1992-10-21) claims examples page 2, line 36 - line 47 page 4, line 50 - line 52 page 6, line 47 - page 7, line 45	1,8,9, 11-14
E	EP 1 721 962 A (UNILEVER NV [NL]; UNILEVER PLC [GB]) 15 November 2006 (2006-11-15) claims examples page 2, line 29 - line 35	1,7-15
X	EP 0 913 461 A (SHOWA DENKO KK [JP]) 6 May 1999 (1999-05-06) claims examples page 1, line 34 - line 39 page 2, line 1 - line 32 page 2, line 45 - line 48 page 5, line 1 - line 20	1,7-15
X	GB 1 439 518 A (SANTERRE ORSAN; AIR LIQUIDE) 16 June 1976 (1976-06-16) claims 1,8-10 examples page 1, line 14 - line 17 scheme (1) on page 2 page 3, line 127 - page 4, line 14 page 3, line 82 - line 88 page 4, line 27 - line 31	1,6-11, 14
X	US 4 349 447 A (NOGUCHI TATSUHIKO ET AL) 14 September 1982 (1982-09-14) column 1, line 5 - line 15 column 2, line 3 - line 13 column 2, line 32 - line 56 claim 1 examples column 7, line 10 - line 42	1,6-9,11
X	WO 99/02636 A (PROCTER & GAMBLE [US]) 21 January 1999 (1999-01-21) claims 1,7 examples page 8, paragraph 2 - last paragraph	1,6-15
X	US 5 977 053 A (GROTH TORSTEN [DE] ET AL) 2 November 1999 (1999-11-02) cited in the application claims 1,5,6 examples column 4, line 47 - line 64	1,6-9,15

-/--

2

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 5 824 630 A (CHRISTIE JULIE ANN [GB] ET AL) 20 October 1998 (1998-10-20) claim 1 examples column 17, line 60 - line 62 page 11, line 37 - page 12, line 11	1,6-9, 11-15
X	EP 0 659 871 A1 (PROCTER & GAMBLE [US]) 28 June 1995 (1995-06-28) claims examples page 2, line 39 - page 3, line 2	1,6,8,9, 11-13
X	GB 2 311 536 A (PROCTER & GAMBLE [US]) 1 October 1997 (1997-10-01) claims 1-12 examples page 5, paragraph 3 - page 8, paragraph 1 page 32, last paragraph - page 33, paragraph 2 page 48, last paragraph	1,2,7-15
X	US 5 786 313 A (SCHNEIDER JUERGEN [DE] ET AL) 28 July 1998 (1998-07-28) claim examples column 1, line 40 - line 47 column 4, line 65 - line 67 column 6, line 39 - line 44 column 9, line 20 - line 25	1,7-10, 14
X	WO 97/49792 A (BENCKISER GMBH JOH A [DE]) 31 December 1997 (1997-12-31) claims examples page 10, paragraph 5 - page 11, paragraph 2 page 6, paragraph 4 - page 7, paragraph 2	1,7-15
X	US 5 929 012 A (DEL DUCA VALERIO [IT] ET AL) 27 July 1999 (1999-07-27) claims 10,15-17 examples column 6, line 12 - line 37	1,6-10, 14
X	EP 0 882 786 A1 (KAO CORP [JP]) 9 December 1998 (1998-12-09) claim 1 examples page 2, line 7 - line 9 page 2, line 50 - line 57 page 3, line 13 - line 52 page 6, line 51 - page 8, line 4	1,6-15

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/004149

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2006/106332 A (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB]; PREUSCHEN JU) 12 October 2006 (2006-10-12) examples 1,5	1,2, 5-13,15
X	WO 97/36990 A (PROCTER & GAMBLE [US]; ADDISON MICHAEL CROMBIE [GB]; KNOX RHONA ALEXAN) 9 October 1997 (1997-10-09) claims examples page 48, last paragraph page 30, paragraph 2 - paragraph 3	1,2,7-15

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

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2006/004149

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9813467 A	02-04-1998	AU 715749 B2	10-02-2000
		AU 4302197 A	17-04-1998
		BR 9711419 A	24-08-1999
		CA 2264555 A1	02-04-1998
		EP 0929657 A1	21-07-1999
US 6194373 B1	27-02-2001	NONE	
JP 2001003089 A	09-01-2001	NONE	
DE 3829847 A1	15-03-1990	AU 620640 B2	20-02-1992
		AU 4095689 A	08-03-1990
		CA 1326427 C	25-01-1994
		EP 0356974 A2	07-03-1990
		ES 2042913 T3	16-12-1993
		JP 2163200 A	22-06-1990
		US 4997587 A	05-03-1991
EP 0550087 A	07-07-1993	AU 3051592 A	01-07-1993
		BR 9205187 A	06-07-1993
		CA 2086024 A1	01-07-1993
		JP 6080999 A	22-03-1994
		TR 26874 A	22-08-1994
US 4132735 A	02-01-1979	NONE	
WO 2005090541 A	29-09-2005	CA 2559829 A1	29-09-2005
		EP 1725643 A1	29-11-2006
WO 0058228 A	05-10-2000	AU 774805 B2	08-07-2004
		AU 4027100 A	16-10-2000
		CA 2368445 A1	05-10-2000
		EP 1165450 A1	02-01-2002
US 5968884 A	19-10-1999	NONE	
US 3875070 A	01-04-1975	CA 987437 A1	13-04-1976
		CH 571058 A5	31-12-1975
		DE 2161554 A1	20-06-1973
		FR 2162401 A1	20-07-1973
		GB 1408780 A	08-10-1975
		IT 973947 B	10-06-1974
		JP 48066111 A	11-09-1973
		NL 7216724 A	13-06-1973
EP 0509382 A2	21-10-1992	AT 173007 T	15-11-1998
		CA 2063118 A1	18-10-1992
		DE 69227479 D1	10-12-1998
		DE 69227479 T2	10-06-1999
		ES 2122974 T3	01-01-1999
		US 5362412 A	08-11-1994
EP 1721962 A	15-11-2006	NONE	
EP 0913461 A	06-05-1999	US 5929006 A	27-07-1999
GB 1439518 A	16-06-1976	CH 606409 A5	30-11-1978
		DE 2339888 A1	21-02-1974

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2006/004149

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB 1439518 A		FR	2195594 A1	08-03-1974
		FR	2207869 A2	21-06-1974
		JP	50003979 A	16-01-1975
		SE	401175 B	24-04-1978
US 4349447 A	14-09-1982	CA	1120817 A1	30-03-1982
		DE	3062987 D1	09-06-1983
		EP	0030461 A1	17-06-1981
		JP	1217345 C	17-07-1984
		JP	56081399 A	03-07-1981
		JP	58051994 B	19-11-1983
WO 9902636 A	21-01-1999	NONE		
US 5977053 A	02-11-1999	AT	251211 T	15-10-2003
		AU	703102 B2	18-03-1999
		AU	6067796 A	06-02-1997
		CA	2182158 A1	01-02-1997
		CZ	9602257 A3	12-02-1997
		DE	19528059 A1	06-02-1997
		DK	757094 T3	22-12-2003
		EP	0757094 A2	05-02-1997
		ES	2208709 T3	16-06-2004
		HU	9602096 A2	28-04-1997
		JP	9048995 A	18-02-1997
		NO	963190 A	03-02-1997
		PL	315446 A1	03-02-1997
		PT	757094 T	27-02-2004
US 5824630 A	20-10-1998	NONE		
EP 0659871 A1	28-06-1995	AT	194013 T	15-07-2000
		CA	2138826 A1	24-06-1995
		DE	69424986 D1	27-07-2000
		DE	69424986 T2	08-03-2001
		US	5545352 A	13-08-1996
GB 2311536 A	01-10-1997	CA	2250369 A1	09-10-1997
		EP	0901511 A1	17-03-1999
		WO	9736975 A1	09-10-1997
US 5786313 A	28-07-1998	AT	196921 T	15-10-2000
		AT	257466 T	15-01-2004
		AT	226241 T	15-11-2002
		DE	4319935 A1	22-12-1994
		DK	703971 T3	13-11-2000
		DK	0781762 T3	08-03-2004
		DK	0846753 T3	04-11-2002
		WO	9429421 A1	22-12-1994
		EP	0703971 A1	03-04-1996
		ES	2151551 T3	01-01-2001
		ES	2214562 T3	16-09-2004
		ES	2184955 T3	16-04-2003
		JP	8511255 T	26-11-1996
		JP	3615546 B2	02-02-2005
		JP	2004323533 A	18-11-2004
		US	6005141 A	21-12-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2006/004149

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
			US 6008176	A	28-12-1999
WO 9749792	A	31-12-1997	AT 205250	T	15-09-2001
			CA 2258218	A1	31-12-1997
			EP 0906407	A1	07-04-1999
			ES 2160355	T3	01-11-2001
US 5929012	A	27-07-1999	NONE		
EP 0882786	A1	09-12-1998	DE 69723677	D1	28-08-2003
			DE 69723677	T2	22-04-2004
			WO 9727278	A1	31-07-1997
			JP 3810854	B2	16-08-2006
			JP 9287000	A	04-11-1997
			US 6211141	B1	03-04-2001
WO 2006106332	A	12-10-2006	NONE		
WO 9736990	A	09-10-1997	CA 2250293	A1	09-10-1997
			EP 0889947	A1	13-01-1999
			GB 2311538	A	01-10-1997