Dishwashing composition and process for washing dishes

(57) The present invention provides a multifunctional machine dishwasher detergent composition being essentially free of phosphates and comprising:

a) at most 10 wt% of surfactant;

b) from 5 to 70 wt% of an amino polycarboxylic compound;

c) from 5 to 40 wt% of citrate;

d) from 0.05 to 3 wt% of a water soluble bismuth salt;

e) from 0 to 5 wt% silicate;

wherein the amount of citrate is from 30 to 70 wt% on the total weight of citrate and amino polycarboxylic compound.

It was surprisingly found that this composition provides a good alternative to phosphate builders and shows good cleaning and glass care performance.
Description

Technical field

[0001] The present invention is in the field of machine dishwashing. More specifically, the invention encompasses automatic dishwashing detergents and their use in a dish washing process.

Background to the invention

[0002] Traditionally, a consumer would use three products to wash dishes in an automatic dishwashing machine. Salt would be added to the salt compartment to soften water. A dishwashing detergent composition would serve to clean the articles, and a rinse aid would be used in the final steps of the dishwashing process to avoid streaks and smears on the articles.

[0003] In recent years these traditional products have at least partly been replaced by products that are referred to as "2 in 1" products and "3 in 1" products.

[0004] "2 in 1" products already comprise the salt-function built into the product and therefore in use, there is no longer a need to add salt to the salt compartment of the washing machine. A rinse aid is still separately added.

[0005] "3 in 1" products obviate the need for salt addition and rinse aid addition. The three desired functions of cleaning, rinsing and softening are included in one product.

[0006] "4 in 1" products comprise, in addition to the ingredients of the "3 in 1" products, a glass protection agent.

[0007] All these products are further referred to as multifunctional compositions.

[0008] This product shift has greatly improved the ease of handling for consumers.

[0009] Currently most commercial "2 in 1" and "3 in 1" products comprise a builder. The builder system is preferably watersoluble. A builder generally serves to improve and extend the action of surfactant. A builder may provide this contribution in a number of ways, e.g. by binding of calcium and magnesium ions, binding of transition metal ions, peptisation and suspension of soil in solution, provision of alkalinity and structuring/solubilising powder. The binding of calcium and magnesium is the most relevant function among these.

[0010] The most widely known builder is sodium tripolyphosphate. A well known drawback of this builder is that it contains phosphorus. Many attempts have been made to (partly) replace this builder with one that is more environmentally friendly but still shows the desired functionality.

[0011] Examples of suitable replacers that have been suggested are carbonate, citrate, zeolite, silicate and amino polycarboxylic compounds such as methylglycine diacetic acid (MGDA) and variants thereof e.g. NTA (nitrile triacetic acid), GDA (glutamic diacetic acid), DPA (dipicolinic acid) and IDS (imino disuccinic acid). In this context, the acids and corresponding salts thereafter are included in the definitions.

Although these may be suitable in general in a variety of products to (partly) replace phosphate, some of them have drawbacks when used in multifunctional compositions.

[0012] The most common replacer of phosphate builder is citrate. A drawback of the inclusion of citrate is that its functionality is not optimal in a hard water environment. Natural water contains calcium and magnesium ions which can act as counterion to carbonate. Under certain conditions this may lead to the precipitation of calcium/magnesium carbonate. This precipitate is white on glass and washware and is certainly not desired by consumers. The level of these cations is referred to as the total hardness of water which is expressed as milligrams of equivalent calcium carbonate (Mw 100) per liter (ppm).Reference is made to L.S. Clesceri et al, Standard methods for the examination of water and wastewater, 17th edition, American Public Health Association, Washington DC, 1989. The hardness of natural waters can range from only a few ppm up to over 400 ppm in some areas.

[0013] The inclusion of alternative builders such as amino polycarboxylic compounds is described in EP-B-906,407. We have found that the inclusion of such builders may lead to increased glass corrosion and fading of decorated glass. The alternative builder silicate was found to reduce this fading of decorated glass but led to increased glass corrosion for plain glass.

[0014] In view of these drawbacks of the prior art compositions that are low in phosphate builder content, it is an object of the invention to provide a multifunctional machine dishwash detergent composition which is essentially free of phosphate but still shows good performance on cleaning, scaling, and corrosion reduction. More in particular, it is an object of the invention to provide such a machine dishwash detergent composition which shows good glass care, i.e. a reduction of glass corrosion and/or a reduction of fading of decorated glass.

Summary of the invention

[0015] It has been found that a machine dishwash detergent composition comprising citrate and amino polycarboxylic
compound, and in which the choice of other components and conditions for use is carefully made, leads to a combination of benefits without the negatives indicated, which was not known before.

[0016] We have surprisingly found that a combination of a specific amino polycarboxylic compound, citrate and water soluble salt of bismuth, provides a good alternative to phosphate builders. In this composition it is essential that the level of silicate is below 5 wt%.

[0017] Therefore the invention relates to a multifunctional dishwashing composition for use in an automatic dish washer, said composition being essentially free of phosphates, wherein the composition comprises

a) surfactant in an amount of at most 10 wt%;

b) an amino polycarboxylic compound selected from methylglycine diacetic acid (MGDA) and iminodiacetic acid (IDS), in an amount of from 5 to 70 wt%, preferably 10 to 40 wt%, more preferred from 20 to 30 wt%;

c) citrate in an amount from 5 to 40 wt% on total weight of the composition;

d) from 0.05 to 3 wt%, preferably from 0.1 to 2 wt%, more preferred from 0.2 to 1 wt%, of a water soluble salt of bismuth;

e) from 0 to 5 wt% of silicate,

wherein the amount of citrate is from 30 to 70 wt% on the total weight of citrate and aminopolycarboxylic compound.

[0018] The invention further relates to a method for washing articles in a mechanical dishwashing machine comprising treating the articles with a wash liquor comprising the composition according to the invention.

In another aspect the invention relates to a packaging unit comprising a pack comprising the dishwashing composition according to the invention.

In a further aspect the invention relates to the use of a composition according to the invention in an automatic dishwashing machine so no salt is required for rejuvenation of ion exchange material within the machine.

Detailed description of the invention

[0019] Where in this specification reference is made to citrate or aminocarboxylic compound or another acid, this is intended to encompass the acid, a salt thereof or a combination.

[0020] The compositions according to the invention comprise a builder. The compositions are essentially free of phosphate and therefore another builder is included.

[0021] In the context of the invention, essentially free of phosphate is defined as containing less than 1 wt% phosphate-compound on total weight of the composition. Examples of phosphate containing compounds are tripolyphosphates, hexametaphosphate, orthophosphate, and the alkalimetal (preferably sodium) salts thereof.

[0022] The builder functionality in these compositions is found in the combination of the amino polycarboxylic compound and citrate. To obtain the desired delicate balance between builder functionality, also in a hard water environment, glass corrosion, shading by calcium precipitates, and cleaning, it is essential that the amount of citrate is from 30 to 70 wt% on the total weight of citrate and amino polycarboxylic compound. In a preferred embodiment the amount of citrate is from 40 to 60 wt% on the total weight of citrate and amino polycarboxylic compound.

[0023] The total level of citrate in the compositions is preferably from 10 to 30 wt%, more preferred from 10 to 25 wt%.

The total level of amino polycarboxylic compound is preferably from 10 to 40 wt%, more preferred from 20 to 30 wt% on total weight of the composition.

Citrate is preferably present in the form of its sodium salt.

[0024] Because of the cleaning properties and good performance at decreased pH, the amino polycarboxylic compound is selected from MGDA and IDS. The most preferred type of amino polycarboxylic compound is MGDA.

 Optionally the composition comprises a further builder which may be selected for example from the group comprising alkali metal carbonates, bicarbonates, borates and zeolites.

[0025] The composition comprises from 0 to 5 wt% of silicate.

[0026] In commonly used detergent formulations not according to the current invention, silicate is present in amounts up to 30 wt% or even higher, around 50 wt%. Purpose of the silicate in those known compositions is often to prevent fading of colours on glaze porcelain and decorated glasses via corrosion, as well as on enamel and metal corrosion.

[0027] Surprisingly, it has been found that the amount of silicate present in the composition of the current invention should be far less than 30 wt%, most preferably even as low as possible, while use of the machine dishwash detergent composition of the invention does not lead to negative effects from the reduction or even omission of silicate compounds in said composition. We even found that there is a benefit of reduced glass corrosion for normal glassware, linked to the very low levels, or even absence of silicate.

[0028] With the current invention, there is a maximum amount of silicium compounds in the form of silicate to be present. The total amount of silicate present is 5 wt%.

If any silicate is present in the composition or the process of the current invention, it is preferred that the silicate is chosen from the group of alkali metal silicates. The silicate may provide pH adjusting capability and protection against corrosion.
of metals and against attack on décor on dishware, including fine china and glassware benefits. The ratio of SiO₂ to the alkali metal oxide (M₂O, where M=alkali metal) is typically from 1 to 3.5, preferably from 1.6 to 3, more preferably from 2 to 2.8. Preferably, the alkali metal silicate is hydrous, having from 15% to 25% water, more preferably, from 17% to 20%. As indicated, the silicate levels indicated in the specification are calculated as SiO₂.

[0029] The highly alkali metasilicates can in principle be employed, but in general, yield too high a pH to be suitable for application in the compositions of the current invention. Therefore, the less alkaline hydrous alkali metal silicates having a SiO₂:M₂O ratio of from 2.0 to 2.4 are, greatly preferred. Anhydrous forms of the alkali metal silicates with a SiO₂:M₂O ratio of 2.0 or more are less preferred because they tend to be significantly less soluble than the hydrous alkali metal silicates having the ratio of less than 2.

[0030] From the alkali metal silicates, sodium and potassium, and especially sodium, silicates are preferred. A particularly preferred alkali metal silicate is a granular hydrous sodium silicate having a SiO₂:Na₂O ratio of from 2.0 to 2.4 available from PQ Corporation, named Britesil H20 and Britesil H24. Most preferred is a granular hydrous sodium silicate having a SiO₂:Na₂O ratio of 2.0, in particular for application in machine dishwash detergent compositions applied in powder or tablet form. While typical forms, i.e. powder and granular, of hydrous silicate particles are suitable, preferred silicate particles having a mean particle size between 300 and 900 μm and less than 40% smaller than 150 μm and less than 5% larger than 1700 μm. Particularly preferred is a silicate particle with a mean particle size between 400 and 700 μm with less than 20% smaller than 150 μm and less than 1% larger than 1700 μm.

[0031] Machine dishwash compositions according to the invention comprise less than 5 wt.% of silicate. Preferably, a maximum amount of 4 wt.% silicate, further preferred an amount of less than 3 wt.%, more preferred of less than 2 wt.% is present. Even better visible glass corrosion inhibition results are observed at silicate levels of less than 1.5 wt. %, more desirably less than 0.8 wt.%. Therefore, it is preferred that the level of silicate in the dishwash composition, more particularly, in the water of the wash cycle, is as low as possible. Accordingly, in a specific embodiment of the invention, the machine dishwash detergent composition is substantially free of silicate.

[0032] The composition of the invention comprises a water soluble salt of bismuth. In this patent specification, for any reference made to bismuth or bismuth salt levels, the levels indicated are calculated as bismuth ions, unless indicated otherwise. Where bismuth is mentioned, a soluble salt of bismuth is meant, unless indicated otherwise.

[0033] For the purpose of preventing visible glass corrosion, the level of water soluble bismuth salt in the machine dishwash detergent composition of the invention is less than or equal to 3 wt.%, based on the total composition. Although it has been observed that at very low levels of bismuth, an effect can already be obtained, the composition of the invention contains at least 0.05 wt.%. In a preferred embodiment, the composition of the invention comprises from 0.1 to 2 wt% of the water soluble salt of bismuth. Said concentration ranges are based on the average and recommended amount of detergent composition used per main wash cycle. Machine dishwasher detergent compositions according to the invention may suitably be dosed in the wash liquor at levels of from 2 g/l to 10 g/l.

[0034] Water soluble Bi-salts suitable for use in the detergent compositions of the invention are in particular selected from the group of bismuth acetate, acetate dihydrate, bromide, butyrate, citrate, citrate dihydrate, chloride, iodide, iodide dihydrate, caproate, formate, formate dihydrate, fumarate, gluconate, glycinate, lactate, malate, maleate, nitrate, nitrate trihydrate, nitrate hexahydrate, phenolsulphonate, sulfate monohydrate, sulfate heptahydrate, sulfate hexahydrate, salicylate, succinate, tartrate, valerate, saccharinate, and carboxymethyl oxysuccinate. It is preferred to use a water soluble bismuth salt composition chosen from the group of acetate, formate, and sulfate. Mixtures of any of the salts mentioned can also be used.

[0035] It is preferred that the composition of the current invention, in any embodiment thereof, is substantially free of, and further preferred, does not comprise any aluminum or aluminum compound. Aluminum ions are multivalent, and presence thereof in the composition will result in precipitation of insoluble salts thereof. This is disadvantageous as it will result in deposits on the glaseware.

Surfactants

[0036] In particular suitable surfactant systems for use in the machine dishwash detergent compositions of the current invention comprise ethoxylated and/or propoxylated nonionic surfactants, more preferably selected from nonionic ethoxylated / propoxylated fatty alcohol surfactants having a cloud point in water of 14 °C or less, preferably of 10 °C or less when used in the so called multifunctional systems. For other systems, the indicated restriction is less critical.

In general, preferably less than 5 wt.% of a surfactant is present. Surfactants, within the invention, are components within the classification as described in “Surfactant Science Series”, Vol.82, Handbook of detergents, part A: Properties, chapter 2 (Surfactants, classification), G. Broze (ed.). Examples of suitable nonionic surfactants for use in the invention are found in the low- to non-foaming ethoxylated/propoxylated straight-chain alcohols of the Plurafac® LF series, supplied by the BASF Company and the Syneronic NCA series supplied by ICI/ Uniqema. Also of interest are the encapsulated ethoxylated alcohols available as the SLF 18 series from BASF/Olin.

[0037] The ethoxylated and/or propoxylated nonionic surfactants are present at levels of at least 0.5 wt.%, more
preferably 1 to 5 wt.% of the total composition.

If an anionic surfactant is used the total amount thereof present should be at levels of less than 5 wt.%, and preferably at levels of 2 wt.% or below. Furthermore, if any anionic surfactant is present, it is preferred that an antifoam agent to suppress foaming is present.

**Enzymes**

Enzymes may be present in the compositions of the invention. Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, peptidases, amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of biochemical soils and stains encountered in cleansing situations so as to remove more easily the soil or stain from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removal.

**Bleach Material**

Bleach material is preferably incorporated in the composition.

As bleaching agents both the peroxide bleach agents and the chlorine-releasing agents are suitable for inclusion in the composition. Preferably, the composition of the invention also contains a proteolytic enzyme. Enzymes may be present in a weight percentage amount of from 0.2 to 7% by weight.

**Anti-tarnishing Agents**

Anti-tarnishing agents such as benzotriazole and those described in EP 723 577 (Unilever) may also be included.

**Optional Ingredients**

Optional ingredients are, for example, buffering agents, reducing agents, e.g., borates, alkali metal hydroxide and the well-known enzyme stabilisers such as the polyalcohols, e.g. glycerol and borax, crystal-growth inhibitors, threshold agents, perfumes and dyestuffs and the like. In tablets binding agents can be used e.g. modified starches. Reducing agents may be used, e.g., to prevent the appearance of an enzyme-deactivating concentration of oxidant bleach compound. Suitable agents include reducing sulphur-oxy acids and salts thereof. Most preferred for reasons of availability, low cost, and high performance are the alkali metal and ammonium salts of sulphur oxy acids including ammonium sulphite ((NH₄)₂SO₃), sodium sulphite (Na₂SO₃), sodium bisulphite (NaHSO₃), sodium metabisulphite (Na₂S₂O₃), potassium metabisulphite (K₂S₂O₃), lithium hydrosulphite (Li₂S₂O₄), etc., sodium sulphite being particularly preferred. Another useful reducing agent, though not particularly preferred for reasons of cost, is ascorbic acid. The
amount of reducing agents to be used may vary from case to case depending on the type of bleach and the form it is in, but normally a range of about 0.01 wt.% to about 1.0 wt.%, preferably from about 0.02 wt.% to about 0.5 wt.%, will be sufficient.

In a highly preferred embodiment of the current invention, the machine dishwash detergent composition furthermore comprises at least one dispersing polymer. Such polymers have been found to have a beneficial effect on the efficiency of the water soluble zinc salt, in particular, it has been found that such polymers reduce the precipitation of any insoluble zinc salt. Dispersing polymers as referred to in this invention are chosen from the group of anti-spotting agents and/or anti-scaling agents.

Examples of suitable anti-spotting polymeric agents include Acusol 460 ND (ex Rohm & Haas), whereas also synthetic clays, and preferably those synthetic clays which have a high surface area are very useful to prevent spots, in particular those formed where soil and dispersed remnants are present at places where the water collects on the glass and spots formed when the water subsequently evaporates. Antispotting systems such as Acusol 460 ND are advantageous in the so called multifunctional systems.

Examples of suitable anti-scaling agents include organic phosphonates, polyfunctionally-substituted compounds, and mixtures thereof. Particularly preferred anti-scaling agents are organic phosphonates such as α-hydroxy-2-phenyl ethyl diphosphonate, ethylene diphosphonate, hydroxy 1,1-hexyldiene, vinylidene 1,1-diphosphonate, 1,2-dihydroxyethane 1,1-diphosphate and hydroxy-ethylene 1,1-diphosphonate. Most preferred is hydroxy-ethylene 1,1-diphosphonate (EDHP) and 2-phosphonobutane, 1,2,4-tricarboxylic acid (Bayhilib ex Bayer).

Especially preferred are water soluble dispersing polymers prepared from an allyloxybenzenesulphonic acid monomer, a methallyl sulfinic acid monomer, a copolymerizable nonionic monomer and a copolymerizable olefinically unsaturated carboxylic acid monomer as described in US 5 547 612 or known as acrylic sulphonated polymers as described in EP 851 022. Polymers of this type include polyacrylate with methyl methacrylate, sodium methallyl sulphonate and sulphophenol methallyl ether such as Alcosperse 240 supplied by Alco.

Also suitable is a terpolymer containing polyacrylate with 2-acylamido-2 methylpropane sulphonic acid such as Acumer 3100 supplied by Rohm and Haas.

As an alternative, polymers and co-polymers of acrylic acid having a molecular weight between 500 and 20,000 can also be used, such as homo-polymeric polycarboxylic acid compounds with acrylic acid as the monomeric unit. The average weight of such homo-polymers in the acid form preferably ranges from 1,000 to 100,000 particularly from 3,000 to 10,000 e.g. Sokolan™ PA 25 from BASF.. Also suitable are polycarboxylates co-polymers derived from monomers of acrylic acid and maleic acid. The average molecular weight of these polymers in the acid form preferably ranges from 4,000 to 70,000.

Mixture of anti-scaling agents may be used, particularly useful is a mixture of organic phosphonates and polymers of acrylic acid with methyl methacrylate, sodium methallyl sulphonate.

It is preferable if the level of anti-scaling agent is from 0.2 to 10 wt.% of the total composition, preferably from 0.5 to 5 wt.%, and further preferred 0.5 to 4 wt.%.

Suitable forms for the machine dishwash detergent composition are a powder, tablet, gel or liquid detergent composition, and mixtures thereof. Preferably the compositions are unit dose compositions such as tablets or gel particles. Most preferred the compositions are in the form of tablets. Unit dose compositions such as tablets or gels may be wrapped in a water soluble wrap for easy handling.

In a preferred embodiment, the composition according to the invention comprises a rinse aid composition/ingredient.

Rinse aid ingredients are ingredients that effect that final appearance of the table ware that is washed. Examples of such ingredients are commercially available under the tradenames SLF, Acusol and Alcosperse.

In a further aspect, the invention relates to a method for washing articles in a mechanical dishwashing machine comprising the steps of treating the articles with a wash liquor comprising a dishwashing composition according to the invention as specified above, wherein minimal rejuvenation of ion exchange material within the machine is needed.

In this embodiment there is no need for the consumer to add salt to the designated salt compartment in the machine.

Also advantageous in the so called multifunctional systems.

In another aspect, the invention relates to a packaging unit comprising a pack comprising the dish wash composition according to the invention and optionally a separate pack with rinse aid composition, wherein the packaging unit contains instructions not to add salt to the machine. In a more preferred embodiment the packaging unit does not contain a rinse aid and the pack comprising the dish wash composition contains further instructions not to add rinse aid.
to the machine.

Description of figures

[0062] Figure 1 shows the chemical structure of MGDA and IDS.

[0063] The following non-limiting examples are provided as an illustration to the invention.

Examples

Example formulation

[0064] Overall composition

<table>
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<tr>
<th>Component</th>
<th>Parts</th>
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<tbody>
<tr>
<td>Premix</td>
<td></td>
</tr>
<tr>
<td>MGDA (Trilon M granule, ex BASF)</td>
<td>20</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>13</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>5</td>
</tr>
<tr>
<td>Sodium disilicate</td>
<td>2</td>
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<tr>
<td>Sodium sulphate</td>
<td>10.12</td>
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<td>Sodium citrate</td>
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<td>Benzotriazole</td>
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<td>Perfume</td>
<td>0.16</td>
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<td>Dye solution</td>
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<td>Postdose</td>
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<tr>
<td>Sodium percarbonate</td>
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<td>TAED (83%)</td>
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<tr>
<td>Protease/Amylase Enzymes</td>
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<tr>
<td>Manganese catalyst granule</td>
<td>0.9</td>
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<tr>
<td>Dequest™ 2016D granule (phosphonate)</td>
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<tr>
<td>Acusol™ 460ND (polyacrylate polymer)</td>
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<tr>
<td>Sokalan™ PA25CL (maleic acid, acrylic acid copolymer from BASF)</td>
<td>3</td>
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<tr>
<td>Zinc sulphate monohydrate</td>
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Method of preparation:

[0065] First the powder-form premix was fed into a Lödige™ ploughshare mixer, then the liquid components were sprayed onto this powder through a one-phase nozzle, and finally the post-dose components were admixed.

[0066] From this composition 18 gram rectangular tablets were produced in a Korsch™ rotary press, at a speed of approx. 11,000 tabs/hr, and a compaction force of between 40 and 80 kN. Cross section of the tablets was 26 x 36 mm.

Claims

1. A multifunctional dishwashing composition for use in an automatic dish washer, said composition being essentially free of phosphates, wherein the composition comprises
a) surfactant in an amount of at most 10 wt%;
b) amino polycarboxylic compound selected from methylglycine diacetic acid (MGDA) and iminodiacetic acid (IDS), in an amount of from 5 to 70 wt%;
c) citrate in an amount from 5 to 40 wt%;
d) from 0.05 to 3 wt% of a water soluble salt of bismuth and;
e) from 0 to 5 wt% silicate,

wherein the amount of citrate is from 30 to 70 wt% on the total weight of citrate and amino polycarboxylic compound.

2. A dishwashing composition according to claim 1, wherein the amino polycarboxylic compound comprises MGDA.

3. A dishwashing composition according to claim 1 or 2, wherein the composition comprises a rinse aid ingredient.

4. A dishwashing composition according to any of claims 1-3, which is essentially free of silicate.

5. A dishwashing composition according to any of claims 1-4, wherein the amount of citrate is from 40 to 60 wt% based on total weight of citrate and amino polycarboxylic compound.

6. A dishwashing composition according to any of claims 1-6, which comprises an antiscalent polymer.

7. Method for washing articles in a mechanical dishwash machine, comprising treating the articles with a wash liquor comprising a dishwashing composition according to any of claims 1-6, wherein minimal rejuvenation of ion exchange material within the machine is needed.

8. Method according to claim 7, wherein no rejuvenation of ion exchange material is needed.

9. Use of a dishwashing composition according to any of claims 1-6, in an automatic dishwashing machine so no salt is required for the rejuvenation of ion exchange material within the machine.

10. Packaging unit comprising a pack comprising the dish wash composition according to any of claims 1-6 and optionally a separate pack with rinse aid composition, wherein the packaging unit contains instructions not to add salt to the machine.

11. Packaging unit according to claim 10 which does not contain a separate pack with rinse aid composition, wherein the packaging unit contains instructions not to add salt and rinse aid to the machine.
FIGURE 1

IDS (Limo Di Succinic Acid):

\[ R'''' \quad \text{CH} \quad \text{H} \quad \text{CH} \quad \text{COOH} \]

\[ R''' \quad \text{CH}_2 \quad \text{COOH} \]

MGDA (Methyl Glycine Di Acetic Acid):

\[ R'' \quad \text{CH} \quad \text{H} \quad \text{CH}_3 \quad \text{COOH} \]

\[ R' \quad \text{CH}_2 \quad \text{COOH} \]

Generic formula:

\[ R''' \quad \text{CH} \quad \text{N} \quad \text{CH} \quad \text{R'} \]
## DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
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<th>CLASSIFICATION OF THE APPLICATION (IPC)</th>
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<td>Y</td>
<td>POTTHOFF-KARL B ET AL: &quot;SYNTHESE ABBAUBARER KOMPLEXBILDNER UND IHRE ANWENDUNG IN WASCHMITTEL- UND REINIGERFORMULIERUNGEN&quot; SOFW-JOURNAL SEIFEN, ÖLE, FETTE, WACHSE, VERLAG FUR CHEMISCHE INDUSTRIE, AUGSBURG, DE; vol. 122, no. 6, 1 May 1996 (1996-05-01), pages 392-394, 396, XP000587160 * figures 14,15 *</td>
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<td>A</td>
<td>US 6 165 970 A (WILLIAMS ET AL) 26 December 2000 (2000-12-26) * column 17; example 1 *</td>
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The present search report has been drawn up for all claims

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<td>Munich</td>
<td>14 August 2006</td>
<td>Pfannenstein, H</td>
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**CATEGORY OF CITED DOCUMENTS**

- **X**: particularly relevant if taken alone
- **Y**: particularly relevant if combined with another document of the same category
- **A**: technological background
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- **P**: intermediate document
- **T**: theory or principle underlying the invention
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- **L**: document cited for other reasons
- **M**: member of the same patent family, corresponding document
This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on 14-08-2006.

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<tr>
<td>WO 9749792 A</td>
<td>31-12-1997</td>
<td>AT 205250 T</td>
<td>15-09-2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2258218 A1</td>
<td>31-12-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ES 2160355 T3</td>
<td>01-11-2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 2747602 A1</td>
<td>03-05-1978</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FR 2369337 A1</td>
<td>26-05-1978</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IT 1143765 B</td>
<td>22-10-1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL 7711867 A</td>
<td>03-05-1978</td>
</tr>
<tr>
<td>US 6165970 A</td>
<td>26-12-2000</td>
<td>NONE</td>
<td></td>
</tr>
</tbody>
</table>

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 906407 B [0013]
- US 4751015 A [0046]
- EP 0458397 A [0047]
- US 5041232 A [0047]
- US 5047163 A [0047]
- EP 723577 A [0048]
- US 5547612 A [0052]
- EP 851022 A [0052]

Non-patent literature cited in the description