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(54) Machine dishwashing composition containing polyaminoacids as builders.

(57) An improved phosphate-free, particularly phosphorus-free machine dishwashing composition comprises a non-phosphate builder, such as zeolite, alkalimetal citrate, alkalimetal carbonate and bicarbonate, and mixtures thereof, wherein the amount of carbonate and/or bicarbonate if present, does not exceed 50% by weight of the composition, and contains an effective amount of a biodegradable poly-amino acid compound of the formula:

Poly $(X)_n$

wherein each X is independently aspartic acid or salts thereof, glutamic acid or salts thereof, glutamine, asparagine, or mixtures thereof; and n is 3 to 1000.

EP 0 561 452 A1

This invention relates to machine dishwashing compositions. In particular the invention relates to improved phosphate-free machine dishwashing compositions comprising a polyamino acid.

High concentrations of carbonic species (CO^{-}_{3}) during the main washing cycle and final rinse in a dishwasher can lead to the formation of calcium carbonate deposits (scaling) on washed articles, such as dishes, glasses, cutlery etc. and machine parts. Because current zero-P formulations contain inherently weak builders e.g. citrates, carbonates, zeolites, which also have inadequate scale inhibiting properties, the risk of scaling with these products is higher than with conventional sodium triphosphate based products. Tap water with a relatively high water hardness, and insufficient softening in the machine increase the problem dramatically. Other parameters involved in the scaling process are temperature, (high temperature increases deposition) and pH (higher pH appears to increase scaling too).

Scale formation on dishes and machine parts is thus an important problem with phosphate-free machine dishwashing products, especially if they are used in hard water areas and/or if the builder system comprises sodium carbonate and/or if the bleach system comprises sodium percarbonate.

It has now been found that a poly-amino acid compound of the formula:

Poly $(X)_n$

wherein each X is independently aspartic acid or salts thereof, glutamic acid or salts thereof, glutamine, asparagine, or mixtures thereof; and n is from 3 to 1000, preferably from 3 to 500, can be effectively used as anti-scaling agent in phosphate-free machine dishwashing compositions if present in certain critical amounts and if the amount of a carbonate and/or bicarbonate builder in the composition does not exceed 50% by weight of the composition.

Accordingly the invention provides a phosphate-free machine dishwashing composition comprising a non-phosphate builder wherein the amount of carbonate and/or bicarbonate builder if present does not exceed 50% by weight of the composition, and containing at least more than 1%, preferably at least 2% up to 10% by weight of a poly-amino acid compound of the formula:

poly $(X)_n$

wherein X is independently aspartic acid or salts thereof, glutamic acid or salts thereof, glutamine, asparagine, or mixtures thereof, and n is 3 to 1000, preferably from 3 to 500.

In the above formula the X amino acids may be entirely comprised of any one of the X group i.e. polyaspartates, polyglutamates, polyglutamines, polyasparagines, or they may be any combination of members of the group, e.g. poly $(Asp)_5(Glu)_5$.

Builder materials (phosphates and non-phosphate builder materials) are well-known in the art and many types of organic and inorganic compounds have been described in literature. They are normally used in all sorts of cleaning compositions to provide alkalinity and buffering capacity, prevent flocculation, maintain ionic strength, extract metals from soils and/or remove alkaline-earth metal ions from washing solutions.

The builder material usable herein can be any one or mixture of the various non-phosphate builder materials, such as for example the alkalimetal citrates, carbonates and bicarbonates; nitrilotriacetic acid (NTA); dipicolinic acid (DPA); oxydisuccinic acid (ODS); alkenylsuccinates (AKS); and zeolites. They may be present in the composition of the invention in an amount as low as 5% up to about 90% by weight, preferably from 10% to 80% by weight.

Particularly preferred builders are citrates, alkenylsuccinates, carbonates, bicarbonates, zeolites, and mixtures thereof. In using a carbonate and/or bicarbonate builder either alone or in admixture with other builders it should however be observed that the amounts thereof should not exceed 50% by weight of the composition, as explained above.

Compositions containing carbonate and/or bicarbonate builder in an amount of 0% up to 40% by weight are preferred.

Surfactants though not strictly essential may also be present for detergency, soil removal, foam depression and/or as rinse aids. If present they can be used in an amount of up to about 60% by weight depending upon their type and properties. Normally in a properly built or highly built composition as is conventional, only small amounts of low-to non-foaming nonionic surfactant in the order of 0.1-5% by weight are preferably used, to aid detergency and particularly to suppress excessive foaming caused by some protein soil. Higher amounts i.e. 5-60% by weight of highly detersive surfactants, such as the high HLB nonionic surfactants, the anionic sulphate or sulphonate surfactants and the alkyl polyglycoside class of surfactants, may be used in normally lower builder containing active-based compositions.

The composition of the invention may and preferably further contains one or more of the following specialized components for specific purposes during the multi-step wash cycle typical for machine dishwashing compositions:

Alkalimetal silicate, preferably sodium silicate at a level of from about 1 to about 40% by weight, preferably from 5 to 35% by weight. This material is employed as a cleaning ingredient, source of alkalinity, metal corrosion inhibitor and protector of glaze on china tableware. Especially effective is sodium silicate having a mol ratio of SiO_2:$Na_2O$of from about 1.0 to about 3.3., preferably from about 1.8 to about 2.5, normally referred to as sodium disilicate.

Bleach system - If present the amount will preferably lie in a range from 1 to 30% by weight. Alkali metal hypochlorite may be incorporated in liquid compositions. Other chlorine bleaches which may be incorporated are alkali metal salts of di- and tri-chloro and di- and tri-bromo cyanuric acids.

Preferred bleaches are the peroxygen bleaches, such as sodium perborate (tetra- or monohydrate) or sodium percarbonate. These are preferably used in conjunction with a bleach activator which allows the liberation of active oxygen species at a lower temperature. Numerous examples of activators of this type, often also referred to as bleach or peracid precursors, are known in the art. Preferred bleach activators are tetraacetyl ethylene diamine (TAED), glucose pentaacetate (GPA) and the mono-long chain acyl tetraacetyl glucoses as disclosed in WO 91/10719, but other activators such as choline sulphophenylcarbonate (CSPC) as disclosed in US Patents 4,751,015 and 4,818,426 can be used. The amounts of sodium perborate or percarbonate and bleach activator in the compositions preferably do not exceed 20% and 10% by weight respectively.

Another peroxygen bleach is potassium monopersulphate. Further peroxygen bleaches which may be used are the organic peroxyacids and their metal salts. Typical peroxyacids include:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-α-naphthoic acid;

(ii) aliphatic and substituted aliphatic monoperoxy acids, e.g. peroxylauric acid and peroxystearic acid;

(iii) 1, 12-diperoxydodecanedioic acid (DPDA);

(iv) 1, 9-diperoxyazelaic acid;

(v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

(vi) 2-decyldiperoxybutane-1,4-dioic acid; and

(vii) phthaloylamido peroxycaproic acid (PAP)

Instead of or together with said bleach activators, a bleach catalyst, such as the manganese complexes of EP-A-458,397 and the sulphonimines of US Patents 5,041,232 and 5,047,163 may also be added.

Enzymes - Amylolytic and proteolytic enzymes are normally used. The amylolytic enzymes usable herein can be those derived from bacteria or fungi. Preferred amylolytic enzymes are those prepared and described in GB Patent No. 1,296,839, cultivated from the strains of Bacillus licheniformis NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11945, ATCC 8480 and ATCC 9945 A. Examples of such amylolytic enzymes are those produced and distributed under the Trade-names of SP-95® and Termanyl® by Novo Industri A/S, Copenhagen, Denmark. These amylolytic enzymes are generally presented as granules and may have enzyme activities of from about 2 to 10 Maltose units/milligram. They may be present in the composition of the invention in amounts such that the final composition has amylolytic enzyme activity of from 10^3 to 10^6 Maltose Units/Kilogram.

The amylolytic activity as referred to herein can be determined by the method as described by P. Bernfeld in "Method of Enzymology" Volume I (1955) page 149.

The proteolytic enzymes usable herein are for example the subtilisins which are obtained from particular strains of B. Subtilis and B. licheniformis, such as the commercially available substilisins Maxatase® supplied by Gist-Brocades NV, Delft, Holland, and Alcalase®, supplied by NOVO Industri A/S Copenhagen, Denmark. Particularly suitable are proteases obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available from NOVO Industri A/S under the Trade names of Esperase® and Savinase®. The preparation of these and analogues enzymes is described in GB Patent No. 1,243,784. These enzymes are generally presented as granules, e.g. marumes, prills, T-granulates etc., and may have enzyme activities of from 500 to 1700 Glycine Units/mg. The proteolytic enzyme activity can be determined by the method as described by M.L. Anson in "Journal of General Physiology" Vol. 22 (1938), page 79 (one Anson unit/gram = 733 Glycine Units/milligram).

In the compositions of the invention proteolytic enzymes may be present in amounts such that the final composition has proteolytic enzyme activity of from about 10^6 to 10^8 Glycine Units/Kilogram.

Other enzymes, such as lipolytic enzymes may also be incorporated to improve fat removal. Typical examples of commercial lipolytic enzymes are Lipase YL, Amano CE, Wallerstein AW, Lipase My, and Lipolase ex Novo Ind.

Other optional ingredients that can be further included in minor amounts are clay minerals, particularly the layered clay minerals to reduce film- and spot formation on washed articles. Typical and particularly preferred commercial clay products are the synthetic hectorites manufactured and supplied by Laporte Industries Ltd, England as Laponite® clays e.g. Laponite S, Laponite XLS, Laponite RD and Laponite RDS. Zinc salts, both soluble and insoluble zinc salts, can also be incorporated as adjuncts for minimizing glass corrosion.

An inert particulate filler especially sodium sulphate may also be incorporated, though in compact powdered composition it should desirably be omitted as practically possible.

The poly-amino acid compound

The poly-amino acid compounds as used in the present invention are homo-polymers of aspartic acid, glutamic acid, glutamine or asparagine, or copolymers of said amino-acids in any combination, and wherein the amino acids can be in the L, D or L/D form. Preferably n is from 5-150, more preferably from 10-100.

Preferred compounds are the poly-aspartates and polyglutamates because of their commercial availability e.g. from the Sigma Chem. Corp. and from the Ajinomoto Company. Cygnus®-32 is a poly-amino acid product containing about 40% by weight of polyaspartates, supplied by the Cygnus Corporation, USA.

The other poly-amino acids according to the invention may be preferred for other reasons.

As indicated hereinabove the amount of poly-amino acid compound usable according to the invention should be at least more than 1% by weight, preferably at least 2% by weight, up to 10% by weight of the composition, which will deliver in the wash liquor a poly-amino acid concentration of from about 30 to 300 ppm.

It is very important that this range should be adhered to since at lower concentrations no observable effect on glass appearance can be achieved, especially at higher carbonate contents, whereas at concentrations higher than 10% by weight the effect appears to be negated by an other undesirable phenomenon i.e. the formation of a bluish film on glass and metal surfaces, believed to be caused by very fine crystals of calcium carbonate adhering to the glass and metal surfaces. A preferred range for achieving the best results is from 3% to about 8% by weight of the poly-amino acid in the composition.

Used at these levels the poly-amino acid compound according to the invention are effective in reducing scale built-up on glasses, dishes etc., thereby improving the glass appearance. They have the further advantages of being biodegradable and capable to inhibit metal corrosion.

Accordingly machine dishwashing compositions falling within the scope of the present invention may contain the following components:

Composition	% by weight	
	General	Preferred
Total Non-phosphate builder	5 - 90	10 - 80
Na_2CO_3/$NaHCO_3$	0 - 50	0 - 40
Surfactant	0 - 60	0.1 - 5
Alkalimetal silicate	0 - 40	1 - 40
Bleach system	0 - 30	1 - 30
Amylolytic enzyme	0 - 10^6 MU/Kg	103-10^6 MU/Kg
Proteolytic enzyme	0 - 10^8 GU/Kg	10^6-10^8 GU/Kg
Poly-amino acid	>1 - 10	2 - 10
Clay	±	±
Zinc salt	±	±
Filler	±	-
pH	8.5- 11.5	9.5 - 11.0

The invention will now be illustrated by way of the following non-limiting Examples.

Examples I and II

Set-up scaling experiments.

The build-up of scale (calcium carbonate) on dishes in a machine dish wash process was investigated in small scale model scaling experiments. The wash cycli in such experiments are simulated by heating a

washing solution containing pre-weighed glass slides. The weight increase of these slides during a 9 cycle build-up experiment is considered to be due to the deposition scale. A combined main wash and final rinse experiment was used to study scale protection with a main wash composition.

Main wash/final rinse experiment

In a 3 liter beaker glass 2.7 gram of a composition is added to 1.5 litre of hard water. This water is made by adding calcium chloride, magnesium chloride and sodium bicarbonate to demineralized water in such amounts that a total water hardness of 40 degrees French[1](molar ratio Ca/Mg:4/1) and a temporary (bicarbonate) hardness of 32 degrees French[2]is obtained. After placing pre-weighed glass slides (5x5x0.1 cm) in this solution the temperature is raised from 20 to 65 °C at a rate of 2.5 °C per minute, and kept constant at 65 °C for 12 minutes. This temperature profile simulates a main wash cycle and is obtained using a submerged electrical heating element and a programmable temperature controller. At the end of this cycle the slides are taken out of the solution. One slide is used for the determination of the scale formation during this cycle and is replaced by a new slide. Subsequently a final rinse cycle is simulated by adding the remaining slides to 1.5 litre of water of the same hardness. At the same time 1.5 ml of the main wash solution (simulating a 1/1000 carry-over from the main wash) is added. This final rinse solution is then heated from 20 to 70 °C (2.5 °C/min) and kept isothermal for 10 minutes. At the end of this cycle again one slide is removed for analysis and replaced by a new one. Generally this procedure is repeated nine times.

Mainwash composition (% by weight)					
	I(a)	I(b)	I(c)	II(a)	II(b)
sodium citrate	43.0	43.0	43.0	20.0	20.0
sodium carbonate	-	-	-	28.2	28.2
sodium bicarbonate	-	-	-	20.0	20.0
sodium disilicate	34.0	34.0	34.0	25.0	25.0
sodium perborate mono-hydrate	6.8	6.8	6.8	6.8	6.8
TAED	4.2	4.2	4.2	4.2	4.2
Savinase® proteolytic enzyme	(1.7)	(1.7)	(1.7)	(1.7)	(1.7)
Termamyl® amylolytic enzyme	(1.7)	(1.7)	(1.7)	(1.7	(1.7)
Laponite® clay	1.7	1.7	1.7	1.7	1.7
Nonionic surfactant	1.7	1.7	1.7	1.7	1.7
Poly $(ASP)_n$ ex Bayer ($_n$ = 32)	5.0	-	-	-	-
Cygnus®-32 (40% Poly-$Asp)_n$($_n$ = 156)	-	12.5	-	12.5	18.7
$Poly(Glu)_n$ ($_n$ = 146)	-	-	5.0	-	-

The results are given in the following Table.

1) 1°FH (Ca and/or Mg) is equivalent to 0.1 mmol/l $CaCO_3$.

2) 1°FH (HCO_3) is equivalent to 0.2 mmol/l $NaHCO_3$.

Table

Scale build-up on glasses after 9 wash cycli	
Composition	weight increase in mg/slide
I(a) (+ poly-amino acid)	10
I(b) (+ poly-amino acid)	17
I(c) (+ poly-amino acid)	42
I (- poly-amino acid)	73
II(a) (+ poly-amino acid)	48
II(b) (+ poly-amino acid)	43
II (- poly-amino acid)	52

The above results show that in all cases scale formation is inhibited by the presence of poly-amino acid. The above data also shows the negative effect of high carbonate/bicarbonate builder content and the lower effectivity of Cygnus-32 (an impure product) over the purer polyaspartate product ex Bayer.

Claims

1. A phosphate-free machine dishwashing composition comprising a non-phosphate builder wherein the amount of carbonate and/or bicarbonate builder, if present, does not exceed 50% by weight of the composition, and at least more than 1% up to about 10% by weight of a poly-amino acid compound of the formula:

poly $(X)_n$

wherein each X is independently aspartic acid and salts thereof, glutamic acid and salts thereof, glutamine, asparagine, or mixtures thereof, and n is 3 to 1000.

2. A composition according to claim 1, characterized in that it comprises at least 2% by weight of said polyamino acid compound.

3. A composition according to claim 2, characterized in that it comprises from 3% to about 8% of said polyamino acid compound.

4. A composition according to claim 1, 2 or 3, characterized in that n is 3 to 500.

5. A composition according to claim 4, characterized in that n is 5 to 150.

6. A composition according to claim 5, characterized in that n is from 10 to 100.

7. A composition according to any of the above claims 1-6, characterized in that it comprises a non-phosphate builder selected from the group consisting of citrates, alkenylsuccinates, carbonates, bicarbonates and zeolites, and mixtures thereof.

8. A composition according to any of the above claims 1-7, characterized in that it comprises from 0-40% by weight of a carbonate and/or bicarbonate builder.

9. A composition according to any of the above claims 1-8, characterized in that it comprises from 5% to about 90% of non-phosphate builder.

10. A composition according to claim 9, characterized in that it further comprises:
b) from 0-60% by weight of a surfactant;
c) from 0-40% by weight of an alkalimetal silicate;
d) from 0-30% by weight of a bleach system; and
e) optionally enzymes.

11. A composition according to claim 10, characterized in that it comprises:
a) from 10-80% by weight of non-phosphate builder;
b) from 0.1-5% by weight of a low- to non-foaming nonionic surfactant;
c) from 1-40% by weight of alkalimetal silicate;
d) from 1-30% by weight of a peroxygen bleach system; and
e) amylolytic enzyme and proteolytic enzyme in amounts such that the composition has amylolytic enzyme activity of from 10^3 to 10^6 Maltose Units/Kilogram and proteolytic enzyme activity of from 10^6 to 10^8 Glycine Units/Kilogram.

12. A composition according to claim 10 or 11, characterized in that said alkalimetal silicate is sodium disilicate having SiO_2:Na_2O mol ratio of from about 1.8 to 2.5.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 20 0670

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 454 126 (MONTEDIPE S.R.L.) * Whole document *	1-12	C11D3/37 C11D3/00
Y	DE-A-3 724 460 (LION CORP) * page 3, line 53 - line 55 * * page 4, line 12 - line 15; examples *	1-12	
Y	EP-A-0 256 366 (BAYER AG) * column 3, line 1 - line 5; claim 8 *	1-12	
P,X	EP-A-0 511 037 (RHONE-POULENC CHEMIE)	1-3,7-12	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	28 MAY 1993	PELLI-WABLAT B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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