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(54) **A phosphate-free automatic dishwashing composition.**

(57) A phosphate-free automatic dishwashing composition comprising nonionic tenside, carboxylic acid, water-soluble alkaline compound and bleach, as well as optionally one or more adjuvants or additives, where the bleach is a chlorine-free, oxygen donating bleach, and where the automatic dishwashing composition comprises carbonate, polycarboxylate, polyfunctional carboxylic acid, silicate, and nonionic tenside. The composition may advantageously be in the form of a tablet. The automatic dishwashing composition has an excellent tea stain removing ability, despite its relatively low alkalinity.

EP 0 504 091 A1

Technical field

The present invention relates to a phosphate-free automatic dishwashing composition comprising nonionic tenside, carboxylic acid, water-soluble alkaline compound and bleach as well as optionally one or more adjuvants or additives.

Background Art

Conventional automatic dishwashing compositions are usually particulate/granular or liquid products, which, when used, produce a washing liquor of highly alkaline pH, frequently between 11 and 12. The commonly applied dosage of such dishwashing compositions is between 30 and 60 g per wash cycle. Conventional dishwashing compositions usually comprise phosphates to soften the water, tensides to loosen food and other undesirable residues, as well as chlorine bleaches. A typical automatic dishwashing composition with chlorine and phosphate may comprise 22% by weight of phosphate, 25% by weight of anhydrous metasilicate, 22.5% by weight of sodium carbonate, 1.5-4.5% by weight of chlorine bleach and 2% by weight of nonionic tensides, based on an amount of 40 g per wash cycle (A.S. Davidson and B. Milwidsky, Synthetic Detergents 1987).

Until now, high alkalinity has been regarded as necessary to obtain adequate detergency, but it entails several drawbacks. Articles of soft metal, such as aluminium, are often attacked by alkaline compositions, said attacks corroding the surfaces. Scratches in porcelain and glass are also exposed to such attacks, resulting in a more penetrating damage. High alkalinity can also damage plastic articles and porcelain glazing. A further disadvantage of high alkalinity is the difficulty connected with incorporating enzymes in the composition. Furthermore, a highly alkaline environment can have a detrimental effect on the automatic dishwashing machine. Contact with a strong base is dangerous, for which reason said compositions may give rise to storage problems in homes with children and/or pets.

A large number of conventional automatic dishwashing compositions contain chlorine bleaches, often causing cutlery to tarnish and stain. This effect becomes more marked with decreasing pH. Moreover, the use of chlorine bleaches in highly alkaline dishwashing compositions has considerable disadvantages with respect to manufacture and storage, due to deterioration of other substances upon direct contact with active chlorine. The stability of a chlorine bleach is always critical, posing additional difficulties, especially in connection with domestic storage and use, as toxic chlorine gases are easily released.

The use of chlorine bleaches has the advantage of significantly diminishing the sensitivity to low washing temperatures, increased water hardness and the presence of heavy metal ions. This has obvious benefits as regards the bleaching effect, since it is easier to formulate less expensive dishwashing compositions with excellent bleaching properties even under demanding conditions, such as low washing temperatures and hard water. However, a great disadvantage is the use of enzymes being absolutely excluded due to the extremely pronounced reactivity (resulting in the excellent bleaching effect). Today, enzymes are regarded as necessary, when amylaceous as well as proteinaceous food residues are to be removed satisfactorily. Said types of residues give rise to problems during a low-temperature or "green" dishwashing programme selected for environmental or financial reasons

Over the years, we have become more and more aware of the environmental disadvantages of phosphates. Intensive work is therefore performed to replace phosphate compounds and other environmentally harmful compounds by substances having a similar effect and being environmentally friendly.

A corresponding development takes place with society as well as the consumer becoming increasingly conscious of the environmental and resource-related consequences of the extensive use of laundry detergent compositions, dishwashing compositions and other detergent compositions. There is a rising demand for dishwashing compositions comprising lesser amounts of environmentally harmful, resource-intensive substances than traditionally used in known dishwashing compositions, said new compositions still displaying a similar or even better cleaning performance.The present invention provides an important step in this direction.

Examples of the best, phosphate-free automatic dishwashing compositions of today include SUN PROGRESS™, a phosphate-free, chlorine-free, non-corrosive automatic dishwashing powder available from Lever, Germany, and "Milde Kraft", another phosphate-free, chlorine-free, non-corrosive powder, marketed in Germany by Benckiser. These known automatic dishwashing compositions still have several disadvantages. The requirement of non-corrosiveness, i.e. a relatively low alkalinity, can only be met at the cost of the good cleaning performance. Thus, said compositions do not meet the requirement of also satisfactorily removing difficult stains, such as coffee or tea stains, when used in small dosages.

The difficulties of finding a replacement for phosphates in automatic dishwashing compositions is illustrated in an article by W. Wichelhaus and H. Andree, "Entwicklungstendenzen bei Maschinengeschirrspülmitteln, Tenside Surf. Det. 27, (1990) 1, page 52-56. Page 55, column 1 reads: "Despite numerous efforts due to environ-

mental considerations, manufacturers of dishwashing compositions did not yet succeed in formulating phosphate-free detergents having a performance spectrum equalling the one of conventional products. The few phosphate-free products available on the market today show first of-all a lack of performance reserve when exposed to extensive soiling or high water hardness."

The above-mentioned article by Wichelhaus and Andree suggests the use of a liquid dishwashing composition to facilitate measuring out suitably low dosages of the dishwashing composition. Another possibility is to manufacture an automatic dishwashing composition in the form of a tablet, as such tablets ensure an easy way of providing a low but sufficient dosage.

The manufacture of such tablets is, however, difficult. It became apparent that an automatic dishwashing composition in powder form might be suitable for removing difficult stains, such as tea stains, but when compressed to tablets, the efficiency as regards removal of tea stains was reduced. A possible explanation of this phenomenon may be that the bleaches necessary for removing coffee and tea stains as well as the bleach stabilizers are quickly dissolved when added to water in the form of a powder. Thus, the bleach concentration quickly reaches a value where the bleaching effect with respect to the above-mentioned difficult stains is at its maximum. When a dishwashing composition is used in the form of a tablet, the bleach dissolves at a lower rate in water, especially under difficult conditions, such as hard water and low temperature. The bleach concentration rises slower over a longer period and does not reach the same maximum value as in pulverulent form. The slow release of the bleach into the washing liquor also increases the tendency of active bleach radicals to be inactivated. Furthermore, the bleach stabilizers display a slow release pattern, so that bleach stabilization becomes uncertain.

EP Publication No. 0.256.148 (Ussat et al.; Joh. A. Benckiser GmbH) discloses a cleaning and lime-removing agent for automatic dishwashing machines. Such a product may, based on the anhydrous form, for instance comprise 60% by weight of citric acid, 38% by weight of amidosulphonic acid, 0.2% by weight of perfume and 1.8% by weight of nonionic tenside, cf. Example 1. The product itself is, however, not a dishwashing composition, but rather intended to remove the kind of depositions formed after conventional use of the automatic dishwashing machine.

DE Publication No. 2.230.453 (Filcek et al.; Benckiser) relates to a basic composition to be used in both washing machines and automatic dishwashing machines. The basic composition comprises 1-40% by weight of citric acid or citrate for each part by weight of nonionic tenside. When the composition is used as a dishwashing composition, it is further combined with 1-30 parts by weight of sodium metasilicate, 0-12 parts by weight of sodium carbonate and 0-4 parts by weight of further substances, such as neutral salt and chlorine bleaches. Said automatic dishwashing composition includes, as mentioned, sodium metasilicate,which means that the dishwashing composition is corrosive.

US-PS No. 3.692.684 (Hentschel) (corresponding to SE accepted printed publication no. 352.652) pertains to detergent compositions, including those for automatic dishwashing machines. The compositions are based on water softeners and detergency-increasing agents comprising alkali metal salts of organic, aliphatic and/or aromatic carboxylic acids and/or anhydrides thereof having a maximum of 8 carbon atoms in the hydrophobic part. Examples of such automatic dishwashing compositions include the one of Example 7 comprising 3 parts nonionic tenside, 3 parts sodium alkylpolyglycolether phosphate, 25 parts sodium acetate, 25 parts sodium sulphate, 30 parts sodium citrate and 14 parts adjuvants, including perfume, colouring, bactericides and water. Hentschel does not mention the dosage of such an automatic dishwashing agent. It has therefore to be assumed that Hentschel has used the conventional, high dosage of approx. 40 g per wash cycle. Neither does Hentschel mention a bleach, for which reason said composition is hardly successful in removing coffee and tea stains satisfactorily.

DE Publication No. 2.323.355 (Dankworth et al.; Benckiser) teaches a phosphate-free automatic dishwashing composition, comprising as sequestrant 5-35% by weight of a mixture consisting of citric acid and a cyclic pentacarboxylic acid. Only chlorine-based bleaches are mentioned as optional bleaches. Dankworth's automatic dishwashing composition moreover comprises 1-95% by weight of water-soluble alkaline compounds, such as sodium metasilicate and sodium hydroxide, cf. the Examples. Such automatic dishwashing compositions are consequently corrosive.

None of the known phosphate-free automatic dishwashing compositions has proven effective enough to remove, for instance, coffee or tea stains, when it is simultaneously required that the composition may not comprise chlorine bleaches, may not act as a corrosive and may only be used at small dosages.

The object of the present invention is to provide a phosphate-free automatic dishwashing agent meeting these requirements.

Description of the invention

The object of the invention is accomplished by a phosphate-free automatic dishwashing composition comprising nonionic tenside, carboxylic acid, water-soluble alkaline compound and bleach as well as optionally one or more adjuvants or additives, characterized by the bleach being a chlorine-free oxygen donating bleach, and by the automatic dishwashing composition comprising

20-150 parts by weight of alkalicarbonate or a mixture of alkalicarbonate and alka libicarbonate,
8-150 parts by weight of polycarboxylate,
20-150 parts by weight of polyfunctional carboxylic acid having 2-10 carbon atoms and at least 2 functional groups selected from the group consisting of carboxyl and hydroxyl,
20-70 parts by weight of sodium silicate in the form of layer silicate or $Na_2O:SiO_2$ in the ratio from 1:0.5 to 1:3.5, and
5-25 parts by weight of nonionic tenside,

per 100 parts by weight of the bleach, the parts by weight being based on the anhydrous product without hydration water.

Advantages of the Automatic Dishwashing Composition According to the Invention:

Due to the low alkalinity the dishwashing composition is easy on the automatic dishwashing machine, plates and cutlery, as well as being environmentally friendly. Low alkalinity also means a considerably reduced risk of corrosive action. Thus, it is no longer necessary to use a child-proof package, as is expected to be introduced in Denmark by law in 1992 for potentially corrosive products.

Due to the chlorine-free oxygen donating bleach there is no risk of release of chlorine during or after dishwashing and storage. It is possible to incorporate enzymes in the dishwashing composition to ensure a considerably improved cleaning performance for proteinaceous and amylaceous food residues. It is furthermore possible to incorporate perfume in the dishwashing composition.

A further advantage of the dishwashing composition is that it can be compressed to tablets without losing the bleaching effect. As mentioned above, tablets ensure a uniformly low dosage and prevent overdosage. The tablet shape also allows for an automatic dosing of the dishwashing composition in automatic dishwashing machines of the future.

The dishwashing composition according to the invention comprises at least 20 parts by weight, such as at least 50 parts by weight, preferably 75 parts by weight, and particularly preferred at least 85 parts by weight of alkalicarbonate or a mixture thereof with alkalibicarbonate per 100 parts by weight of the bleach and not more than 150 parts by weight, such as not more than 140 parts by weight, preferably 115 parts by weight, and particularly preferred not more than 105 parts by weight per 100 parts by weight of the bleach.

The amount of polycarboxylate is at least 8 parts by weight, such as at least 20 parts by weight, preferably 35 parts by weight, and particularly preferred at least 64 parts by weight per 100 parts by weight of the bleach and not more than 150 parts by weight, such as not more than 100 parts by weight, preferably 85 parts by weight, and particularly preferred not more than 78 parts by weight per 100 parts by weight of the bleach.

The polycarboxylate is preferably a polyacrylate and/or a maleic acid/acrylic acid copolymer having a molecular weight of 3,000-150,000.

The amount of polyfunctional carboxylic acid is at least 20 parts by weight, such as at least 33 parts by weight, preferably at least 53 parts by weight, and particularly preferred at least 59 parts by weight per 100 parts by weight of the bleach and not mroe than 150 parts by weight, such as not more than 100 parts by weight, preferably 80 parts by weight, and particularly preferred not more than 73 parts by weight per 100 parts by weight of the bleach.

The polyfunctional carboxylic acid is preferably selected from the group consisting of citric acid, malic acid, tartaric acid, glutaric acid, tartronic acid, gluconic acid, salicylic acid, isoserine diacetic acid, NTA and EDTA.

The amount of sodium silicate is at least 20 parts by weight, such as at least 22 parts by weight, preferably 34 parts by weight, and particularly preferred at least 40 parts, and not more than 70 parts by weight, such as not more than 66 parts by weight, preferably 54 parts by weight, and particularly preferred not more than 48 parts by weight per 100 parts by weight of the bleach.

The sodium silicate is preferably sodium disilicate and/or a so-called clay or "layer silicate", i.e. a silicate, which in Germany is termed "Schichtsilikat".

The amount of nonionic tenside is at least 5 parts by weight, such as at least 7 parts by weight, preferably 11 parts by weight, and particularly preferred at least 13 parts by weight, and not more than 25 parts by weight, such as not more than 22 parts by weight, preferably 19 parts by weight, and particularly preferred not more than 17 parts by weight per 100 parts by weight of the bleach.

The chlorine-free, oxygen donating bleach is preferably a peroxy compound or a perhydrate.

Moreover, the automatic dishwashing composition according to the invention advantageously comprises

10-33 parts by weight of a sequestrant and/or 15-45 parts by weight of a bleach activator per 100 parts by weight of chlorine-free oxygen donating bleach.

The automatic dishwashing composition according to the invention is advantageously manufactured in the form of a tablet.

The automatic dishwashing composition according to the invention is advantageously such that a solution of 1% by weight of said composition in water results in a pH-value of 7-10.5, preferably 8-10.0. This pH-value ensures the non-corrosiveness of the dishwashing composition.

The further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

Detailed Description of the Invention

A distinctive characteristic of the present invention is the polyfunctional carboxylic acid acting like a complex-forming agent during the wash by binding the polyvalent cations in the water and thus stabilizing the washing process, especially the bleaching process. Moreover, a polyvalent carboxylic acid has a positive influence on the dissolving time, in case the automatic dishwashing composition has the form of a tablet, as the polyfunctional carboxylic acid reacts with carbonate ions present by giving off bubbles. Surprisingly, it has been shown that the effervescent effect has a significant influence on the removal of tea and coffee stains.

Examples of polyfunctional carboxylic acids include aliphatic, cyclic and aromatic polyfunctional carboxylic acids having at least one carboxyl group and additionally at least one more carboxyl or hydroxyl group, preferably several such functional groups, selected from the group consisting of COOH and OH. Salts as well as lacton, ester, alkoxylate, amine, diamine and sulphonate derivatives, as well as sulphate compounds thereof, are also included. Preferred salts are alkali metal salts, especially sodium salts.

Especially preferred polyfunctional carboxylic acids are lactic acid, malic acid, tartronic acid, gluconic acid, glutaric acid, citric acid, tartaric acid and salicylic acid, most preferred is citric acid, preferably in the anhydrous form.

A further suitable polyfunctional carboxylic acid may be a mixture of dicarboxylic acids available from BASF™ AG under the trade name SOKALAN™ DCS in the form of a white powder. The product comprises a compound of the formula $COOH(CH_2)_nCOOH$, where n = 2-4.

Examples of suitable chlorine-free oxygen donating bleaches are perhydrates and peroxy compounds, as well as mixtures thereof. Perhydrates preferably include alkali metal compounds of perborates in the form of tetra- or monohydrates, perborax, percarbonates, persilicates, citrate perhydrates as well as perhydrates of urea and melamine compounds. Furthermore, acidic persalts, such as persulphates (e.g. caroates), perbenzoates, and peroxycarboxylic acids, such as peroxyphthalate, magnesium monoperoxyphthalic acid, diperoxyphthalic acid,2-octyl-diperoxysuccinic acid, diperoxydodecane dicarboxylic acid, diperoxyazelaic acid, imidoperoxycarboxylic acid, as well as salts and mixtures thereof. Particularly preferred bleaches are sodium percarbonate and sodium perborate.

With respect to bleach systems reference is made to P. Kuzel and Th. Lieser, Tenside Surf. Det. 27 (1990) 1, page 23-28.

The inventive dishwashing composition may contain alkalicarbonate alone, for example sodium carbonate, or a combination of alkalicarbonate and alkalibicarbonate, for example in the weight ratio from 100:1 to 1:10, calculated as the sodium compounds.

Examples of polycarboxylates used include polymers of acrylic acid, hydroxyacrylic acid, maleic acid, itaconic acid, metaconic acid, aconitic acid, methylene malonic acid, citraconic acid etc., as well as copolymers of said carboxylic acids either with each other or with other ethylenically unsaturated compounds, such as ethylene, propylene, isobutylene, vinyl alcohol, vinylmethyl ether, furan, acrolein, vinyl acetate, acrylamide, acrylonitrile, methacrylic acid or crotonic acid.

The molecular weight of the polycarboxylates may be in the range of 1,000-1,000,000, preferably 2,000-100,000 and most preferred 7,000-30,000.

Regarding the polycarboxylates, reference is made to the article by J. Perner and H.-W. Neumann, "Polycarboxylate bei der Reinigung textiler und nichttextiler Substrate", Tenside Surfactants Detergents 24 (1987) 6, page 334-340.

The sodium silicate used may advantageously be a sodium silicate having a $Na_2O:SiO_2$ ratio of 1:0.5 to 1:3.5, preferably 1:1.9 to 1:3.5, and more preferred of 1:2 to 1:3.5. Suitable sodium silicates include so-called clays or "layer silicates", i.e. compounds having the stoicheiometric composition Na_2SiO_5, each layer consisting

of SiO_4-tetrahedrons. It has been shown that such compounds may complement or completely replace conventional silicates. One of the advantages of clays is their excellent ability to bind magnesium ions, which play an important role in the deposition of lime on the heating elements of an automatic dishwashing machine. A preferred clay is the one sold under the trade name SKS-6 by HOECHST™ AG, Frankfurt am Main, Germany.

Tensides suitable for incorporation in the dishwashing composition according to the invention may be any low-foaming nonionic tenside, especially alkylene oxide adducts (adducts of ethylene oxide (EO), propylene oxide (PO) and/or butylene oxide (BO) and mixtures thereof) with alcohols, thioalcohols, diols, fatty acids, fatty acid amides, alkane sulphonamides, alkyl amines as well as alkyl phenols rendered low-foaming by, for instance, substituting the free hydroxyl groups of the polyalkylene glycolether moieties by an ether or acetal group. Nonionic tensides particularly suitable for incorporation in the automatic dishwashing composition are, for instance, mentioned in GB-PS No. 2.206.601 and the publications cited therein.

It is preferred to use fatty alcohol/EO adducts and/or fatty alcohol/EO/PO adducts, such as PLURAFAC™ LF 403 available from BASF™ AG, UKANIL FM 2136 and SYNPERONIC™ RA 30 available from ICI or DEHYPON™ LT 104 or DEHYDOL™ LS 54 available from Henkel KGaA.

When selecting a nonionic tenside it should be noted that products without chlorine bleaches are not as demanding as regards the choice of stable, low-foaming tensides. In contrast to chlorine bleaches it is thus not necessary to use especially expensive tensides resistant to reactions between chlorine and tenside. Said reactions may result in the disappearance of the low-foaming properties or odoriferous problems.

The tenside may be used in varying amounts, depending on whether adjuvants, such as glycerol, are incorporated at the same time. When the tenside is used without adjuvants, the amount of nonionic tenside is preferably 13-21, more preferred 15-19, for instance approx. 17 parts by weight per 100 parts by weight of the bleach. When adjuvants are added, the preferred amount of nonionic tenside is 9-17, more preferred 11-15, for instance approx. 13 parts by weight per 100 parts by weight of the bleach. The adjuvant may be glycerol in an amount of 2-7, preferably 3-5, parts by weight per 100 parts by weight of the bleach. In some cases the addition of an adjuvant, such as glycerol, may improve the product, for instance as regards storage stability.

The dishwashing composition according to the invention may further comprise a sequestrant having a dispersing and complex-binding (sequestering) effect, such as nitrilotriacetic acid (NTA), isoserine diacetic acid, ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DETPA), hyroxyethylethylene diamine triacetic acid (HEEDTA), ethane-1-hydroxy-1,1-diphosphonic acid (HEDP), ethylene diamine tetra(methylene phosphonic acid) (EDTMP), diethylene triamine penta(methylene phosphonic acid) (DETPMP), aminotrimethylene phosphonic acid (ATMP) as well as phytic acid and its derivatives including salts thereof, especially alkali metal or alkaline earth metal salts. Salts of phytic acid include the dodecane sodium salt of phytic acid (inositolhexaphosphoric acid) available from Sigma Chemical Company, USA. Particularly preferred sequestrants are the disodium and tetrasodium salt, respectively, of ethane-1-hydroxy-1,1-diphosphonic acid, available in the form of a free-flowing powder under the trade names SEQUION 10 NAPDR and DEQUEST™ 2016 D, respectively, from G. Bozetto S.p.A., Filago, Italy, and Monsanto PLC,Great Britain, respectively. Phosphonic acid compounds do not only possess complex-binding properties contributing to i.a. stabilizing the bleaches present, but also, due to their high dispersability, so-called threshold properties, i.e. precipitation-limiting properties.

Some of the above-mentioned sequestrants are polyfunctional carboxylic acids comprising the obligatory carboxyl group and at least one further functional group selected from the group consisting of carboxyl and hydroxyl. Moreover, nitrogen is also present in the molecule. Based on the presence of said functional groups (OH and COOH) it has to be assumed that said sequestrants may be incorporated as the polyfunctional carboxylic acid, a requisite component of the automatic dishwashing composition according to the invention, or as a part thereof. Such compounds are, for instance, isoserine diacetic acid, NTA and EDTA. Isoserine diacetic acid having the formula $(CH_2COOH)_2N\text{-}CH_2CHOHCOOH$ is expected to be marketed by BASF™ AG, Germany, within the next 1-2 years in the form of a liquid product comprising 40% isoserine diacetic acid. The product is expected to be the future substitute for EDTA and can be used in the dishwashing composition according to the invention. If isoserine diacetic acid is considered for use in the inventive dishwashing composition in tablet form, it will be necessary for isoserine diacetic acid to be available in the form of a stable powder with sufficient acidity to react with the alkaline salts, such as alkalicarbonates, thereby releasing carbon dioxide. NTA and EDTA fulfill this condition and can thus advantageously be used in the inventive dishwashing composition both in tablet form and in any other form.

When the dishwashing takes place at low temperatures in the range of 40-60°C, a sufficient bleaching effect is obtained by adding bleach activators. Non-limiting examples thereof include N-acyl compounds and O-acyl compounds, such as acylated amines, diamines, amides, acylated glycolurils, N-acylated cyclic hydrazides, triazoles, urazoles, diketopiperazines, sulphuryl amides, cyanurates and imidazolines, carboxylic acid anhydrides, acylated sugar compounds, acylated ester compounds etc. Especially preferred are tetraacetyl

methylene diamine, tetraacetyl ethylene diamine (TAED) as well as higher homologues thereof, tetraacetyl glycoluril (TAGU), pentaacetyl glucose (PAGE), p-hydroxybenzene sulphonates, sodium nonanoyloxybenzene sulphonate (NOBS) and sodium octanoyloxybenzene sulphonate. Most preferred is TAED in the form of a granulate having an active content of 85-98% by weight.

The bleach activators are described in greater detail in GB-PS No. 2.040.983 and GB-PS No. 1.473.201.

As mentioned above, the automatic dishwashing composition according to the invention is advantageously manufactured in the form of a tablet to be used in a dosage of, for instance, one or two tablets per wash cycle. During manufacture, tablet adjuvants have usually to be added, for instance in the form of sodium acetate, sodium sulfate, starch, glycerol, polyethylene glycol, preferably of a molecular weight of 100-10,000, polyvinyl pyrrolidone (PVP), polyvinyl polypyrrolidone (PVPP) or a stearate compound, such as sodium stearate.

Such tablet adjuvants ensure suitable consistency and granulation.

The tablets are manufactured in a manner known per se. First, a basic powder fraction is mixed, comprising bleach, polyfunctional carboxylic acid, alkalicarbonate, alkalibicarbonte, polycarboxylate, sodium silicate and enzymes. After short stirring for 1-5 minutes the nonionic tenside is sprayed on, whereupon one or more adjuvants are sprayed on or added. Then the mixture is subjected to a final stirring lasting 2-10 minutes. The resulting powder mix is compressed to tablets of a diameter of, for instance, 32 mm in a tablet press (eg. Fette Perfecta 4B). The thickness of the manufactured tablet depends on its desired weight and formulation, and is usually in the range of 13-20 mm. Further examples of manufacturing tablets are disclosed in DE-PS No. 355.626, US-PS No. 328.880 and DE-PS No. 3.827.895.

The invention is described in greater detail below and with reference to the following examples.

Example 1

This example describes an automatic dishwashing composition in pulverulent form to be used in an amount of 18 g dishwashing composition per wash cycle.

	% by weight
Sodium percarbonate	22.0
Sodium carbonate	22.0
SOKALAN™ PA 40	16.0
Citric acid	15.0
Sodium disilicate	10.0
TAED 3711	7.0
PLURAFAC™ LF 403	4.0
TERMAMYL™ 60 T	3.0
ESPERASE™ 6.0 T	1.0

SOKALAN™ PA 40: sodium salt of a polyacrylate in pulverulent form having a molecular weight of approx. 15,000, available from BASF™, Germany.
TAED 3711: tetraacetyl ethylene diamine, available from HOECHST AG, Germany.
PLURAFAC™ LF 403: low-foaming nonionic tenside in the from of an ethoxylated fatty alcohol, available from BASF™, Germany.
TERMAMYL™ 60 T: amylolytic enzyme, available from Novo Nordisk A/S, Denmark.
ESPERASE™ 6.0 T: proteolytic enzyme, available from Novo Nordisk A/S, Denmark.

Example 2

This example illustrates a phosphonate-containing automatic dishwashing composition according to the invention to be used in an amount of 18 g per wash cycle.

	% by weight
Sodium percarbonate	21.0
Sodium carbonate	19.0
SOKALAN™ PA 40	16.0
Citric acid	15.0
Sodium disilicate	10.0
TAED 3711	7.0
DEQUEST™ 2016 D	5.0
PLURAFAC™ LF 403	4.0
TERMAMYL™ 60 T	2.0
ESPERASE™ 6.0 T	1.0

DEQUEST™ 2016 D: tetrasodium salt of 1-hydroxy--ethane-1,1-diphosphonic acid (HEDP), available from MONSANTO, Great Britain.

Example 3

This example relates to a dishwashing composition in the form of a tablet having a weight of 18 g and formulated as the dishwashing composition according to Example 2, apart from citric acid being replaced by an equivalent amount of trisodium citrate dihydrate. This modification increases the alkalinity of the dishwashing composition. The tablet does, however, not possess the advantageous effervescent effect obtained by means of citric acid. The following dishwashing trials have shown that said dishwashing composition displayed a strong tendency to over-foam although the nonionic tenside used was low-foaming.

Comparative trials

pH Measurement

The alkalinity was determined by measuring the pH using 1% aqueous solutions of different dishwashing compositions. The results are shown in the table below:

Dishwashing composition	pH
Milde Kraft	10.8
SUN PROGRESS™ (Lever)	10.6
DE 2.230.453*	12.1
Example 2	9.6
Example 1	9.5

* according to Example 3 in DE 2.230.453.

Washing trials

Comparative trials were carried out under the following trial conditions:
Automatic dishwashing machine: Cylinda E 1500
Temperature: 55°C, no pre-wash
Water hardness: 20°dH
Soiling: in accordance with the guidelines of the IEC (International Electrotechnical Commission)
Number of wash cycles: 12
The results were given points according to the following system:
Each cup, plate, knife, fork etc. was evaluated after each wash cycle using a scale of 1-5 points with 5 as

the best result. The points were given for tea cups as well as for the rest of the porcelain and the cutlery. Finally, the total of points was calculated. The points achieved in the trials appear from the following table, where the possible maximum number of points is 100%.

Average number of points after 12 wash cycles

Dishwashing composition	Tea %	Non-tea %	Total %
Example 1	56	59	56
Example 2	59	58	57
Example 3	20	69	38
Milde Kraft	42	68	61
DE 2.230.453*	89	48	73

*Dishwashing composition according to Example 3 in DE Publication No. 2.230.453, dosage per wash cycle: 40 g.

The dishwashing compositions according to Examples 1, 2 and 3 were used in amounts of 18 g per wash cycle.

"Milde Kraft", a phosphate-free, chlorine-free, non-corrosive product available from Benckiser, was used in an amount of 24 g per wash cycle.

As is apparent from the trials, the dishwashing composition according to DE 2. 230. 453 has fewer points for "non-tea", although its dosage is 40 g per wash cycle. On the other hand, it is better at removing tea stains than the dishwashing composition according to the invention (Examples 1 and 2). However, the product has a high alkalinity of 12.1.

The use of trisodium citrate dihydrate instead of citric acid (Example 3) results in a considerably decreased ability to remove tea stains.

A dosage of 24 g of "Milde Kraft", a representative of the best phosphate-free, chlorine-free, non-corrosive products on the market, does not remove tea stains as well as the dishwashing compositions according to Examples 1 and 2 used in amounts of 18 g per wash cycle.

Examples 4-7

Further examples of the automatic dishwashing composition according to the invention are illustrated in the following Table 1:

Table 1

	% by weight			
Example No.	4	5	6	7
Sodium percarbonate	21.0	21.0	21.0	
Sodium perborate monohydrate				21.0
Sodium carbonate	22.0	19.0	19.0	19.0
SOKALAN PA 40	16.0	16.0	12.0	16.0
Polyfunctional carboxylic acid	15.0	10.0	15.0	15.0
Sodium disilicate			5.0	
SKS-6 (clay)	10.0	10.0	5.0	10.0
TAED 3711	7.0	7.0	7.0	7.0
DEQUEST 2016 D		3.0		
Isoserine diacetic acid		5.0	8.0	3.0
PLURAFAC LF 403	4.0	4.0	4.0	4.0
TERMAMYL 60 T	3.0	2.0	3.0	3.0
ESPERASE 6.0 T	1.0		1.0	
ESPERASE/SAVINASE™ 2.0/2.0 T		2.0		2.0

Examples 8-19

Further dishwashing trials were carried out under the conditions described above using 18 g pr wash cycle. The dishwashing compositions tested are shown in Table 2.

Table 2 also shows the proportions of the essential components as parts by weight per 100 parts by weight of the bleach and the performance scores for tea, non-tea and total.

Table 2

	% by weight			
Example No.	8	9	10	11
Sodium percarbonate	21.0	21.0	21.0	21.0
Sodium carbonate	23.5	25.5	27.5	29.4
SOKALAN PA 40	16.0	16.0	16.0	16.0
Citric acid	15.0	15.0	15.0	7.0
Sodium disilicate	10.5	10.5	10.5	12.6
"Layer silicate"				
Isoserine diacetic acid				
TAED 3711	7.0	5.0	3.0	7.0
PLURAFAC LF 403	4.0	4.0	4.0	4.0
TERMANYL 60 T	2.0	2.0	2.0	2.0
ESPERASE 6.0 T	1.0	1.0	1.0	1.0
Sodium sulphate (filler)				
Total % by weight	100	100	100	100
Parts by weight per 100 parts by weight of the bleach				
Alkalicarbonate	112	121	131	140
Polycarboxylate	70	70	70	70
Polyfunctional carboxylic acid	71	71	71	33
Sodium silicate	40	40	40	48
Bleach activator	30	21	13	30
Nonionic tenside	19	19	19	19
Dishwashing performance score				
Tea	57	35	26	33
Non-tea	58	53	56	57
Total	57	41	37	42

continued

Table 2 (continued)

	% by weight			
Example No.	12	13	14	15
Sodium percarbonate	21.0	21.0	21.0	21.0
Sodium carbonate	20.2	29.4	29.4	14.0
SOKALAN PA 40	16.0	6.8	6.8	16.0
Citric acid	15.0	6.9	15.0	15.0
Sodium disilicate		5.8	5.8	10.0
"Layer silicate"	13.8			
Isoserine diacetic acid				10.0
TAED 3711	7.0	7.0	7.0	7.0
PLURAFAC LF 403	4.0	4.0	4.0	4.0
TERMANYL 60 T	2.0	2.0	2.0	2.0
ESPERASE 6.0 T	1.0	1.0	1.0	1.0
Sodium sulphate (filler)		16.1	8.0	
Total % by weight	100	100	100	100
Parts by weight per 100 parts by weight of the bleach				
Alkalicarbonate	96	140	140	67
Polycarboxylate	70	30	30	70
Polyfunctional carboxylic acid	71	33	71	71
Sodium silicate	53	22	22	38
Bleach activator	30	30	30	30
Nonionic tenside	19	19	19	19
Dishwashing performance score				
Tea	58	32	45	50
Non-tea	57	63	53	56
Total	58	44	47	51

continued

Table 2 (continued)

	% by weight			
Example No.	16	17	18	19
Sodium percarbonate	21.0	21.0	21.0	21.0
Sodium carbonate	23.0	29.4	20.0	22.0
SOKALAN PA 40	8.0	6.8	2.0	11.0
Citric acid	15.0	15.0	15.0	25.0
Sodium disilicate	10.5		5.0	6.0
"Layer silicate"		13.8	23.0	
Isoserine diacetic acid				
TAED 3711	7.0	7.0	7.0	7.0
PLURAFAC LF 403	4.0	4.0	4.0	4.0
TERMANYL 60 T	2.0	2.0	2.0	3.0
ESPERASE 6.0 T	1.0	1.0	1.0	1.0
Sodium sulphate (filler)	8.5			
Total % by weight	100	100	100	100
Parts by weight per 100 parts by weight of the bleach				
Alkalicarbonate	110	140	95	105
Polycarboxylate	35	30	9	48
Polyfunctional carboxylic acid	71	71	71	119
Sodium silicate	40	53	107	23
Bleach activator	30	30	30	30
Nonionic tenside	19	19	19	19
Dishwashing performance score				
Tea	47	46	53	48
Non-tea	55	56	56	55
Total	49	49	54	51

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

Claims

1. A phosphate-free automatic dishwashing composition comprising nonionic tenside, carboxylic acid, water-soluble alkaline compound and bleach as well as optionally one or more adjuvants or additives, characterised by the bleach being a chlorine-free, oxygen donating bleach, and by the automatic dishwashing composition comprising
   20-150 parts by weight of alkalicarbonate or a mixture of alkalicarbonate and alkalicbicarbonate,
   8- 150 parts by weight of polycarboxylate,
   20-150 parts by weight of polyfunctional carboxylic acid having 2-10 carbon atoms and at least 2 functional groups selected from the group consisting of carboxyl and hydroxyl,
   20-70 parts by weight of sodium silicate selected from the group of layer silicate and compounds with the composition $Na_2O:SiO_2$ in the ratio from 1:0.5 to 1:3,5, and
   5-25 parts by weight of nonionic tenside,
   per 100 parts by weight of the bleach, the parts by weight being based on the anhydrous product without hydration water.

2. An automatic dishwashing composition as claimed in claim 1, characterised by comprising:
   75-115 parts by weight of alkalicarbonate or a mixture of alkalicarbonate and alkalibicarbonate,
   57-85 parts by weight of polycarboxylate,
   53-80 parts by weight of polyfunctional carboxylic acid,
   34-54 parts by weight of sodium silicate, and
   11-19 parts by weight of nonionic tenside,
   per 100 parts by weight of the bleach, the parts by weight being based on the anhydrous product without hydration water.

3. An automatic dishwashing composition as claimed in claim 1, characterised by comprising:
   85-105 parts by weight of alkalicarbonate or a mixture of alkalicarbonate and alkalibicarbonate,
   64-78 parts by weight of polycarboxylate,
   59-73 parts by weight of polyfunctional carboxylic acid,
   40-48 parts by weight of sodium silicate, and
   13-17 parts by weight of nonionic tenside,
   per 100 parts by weight of the bleach, the parts by weight being based on the anhydrous product without hydration water.

4. An automatic dishwashing composition as claimed in claim 1, characterised by the chlorine-free, oxygen donating bleach being a peroxy compound or a perhydrate.

5. An automatic dishwashing composition as claimed in claim 1, characterised by the polycarboxylate being a polyacrylate and/or a maleic acid/acrylic acid copolymer having a molecular weight of 3,000-150,000.

6. An automatic dishwashing composition as claimed in claim 1, characterised by the polyfunctional carboxylic acid being selected from the group consisting of citric acid, malic acid, tartaric acid, glutaric acid, tartronic acid, gluconic acid, salicylic acid, isoserine diacetic acid, NTA and EDTA.

7. An automatic dishwashing composition as claimed in claim 1, characterised by the silicate being sodium disilicate.

8. An automatic dishwashing composition as claimed in claim 1, characterised by further comprising 10-33 parts by weight of a sequestrant and/or 15-45 parts by weight of a bleach activator per 100 parts by weight of the bleach, the parts by weight being based on the anhydrous product without hydration water.

9. An automatic dishwashing composition as claimed in claim 1, characterised by being manufactured in the form of a tablet.

10. An automatic dishwashing composition as claimed in claim 1, characterised by a solution of 1% by weight of said composition in water resulting in a pH-value of 7-10.5.

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 92 61 0015.7

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-0 313 144 (UNILEVER NV) *The whole document*	1-10	C 11 D 3/00 C 11 D 3/20
X	EP-A-0 240 315 (KAO CORPORATION) *Page 3, line 26 - line 32; page 4; claim 1*	1-10	
A	EP-A-0 414 197 (JOH. A. BENCKISER GMBH) *The whole document*	1-10	
A	EP-A-0 429 124 (THE PROCTER & GAMBLE COMPANY) *The whole document*	1-10	

TECHNICAL FIELDS SEARCHED (Int Cl.5)

C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
STOCKHOLM	05-06-1992	JÄRVMAN D.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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