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(54) **Machine dishwashing gel composition**

Gelzusammensetzung für Geschirrspülmaschine

Composition gélifiée pour lave-vaisselle

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(56) References cited:
WO-A-95/10588
WO-A-97/31996
JP-A- 7 305 094
US-A- 5 094 771

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The file contains technical information submitted after the application was filed and not included in this specification

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Description

Field of the Invention

[0001] The present invention relates to machine dishwashing gel compositions that deliver high performance cleaning and that do not discolor in storage.

Background of the Invention

[0002] Automatic dishwashing detergents for home use have traditionally been in powder or granulate form. More recently, the marketplace has seen the advent of liquid forms of automatic dishwashing products. Liquids have advantages over powders in their convenience of dispensing or dosing, their enhanced solubility, absence of lump formation or "caking" during storage, and absence of dustiness associated with the powder form.

[0003] Since automatic dishwashing machines contain a dispenser cup normally intended for powders, chemists have been challenged in formulating liquid products of appropriate rheological properties.

[0004] Firstly, the composition must be a uniform mixture to deliver an optimum combination of active ingredients to the wash with each dose. Thus, the liquid must possess physical stability against syneresis or physical separation of its active components during storage.

[0005] Secondly, a liquid product must be compatible with automatic dishwashing equipment presently available to the consumer. Home dishwashers are fitted with a closed cup to house detergent through several cycles preliminary to the wash cycle. Cups in these machines do not seal tightly and do not adequately retain liquids of low viscosity. Excessive leakage leads to underdosing in the wash cycle. Performance may be adversely affected. Consequently, any liquid product must possess high viscosity to be effectively retained in the cup and avoid leakage during cycles preceding that of the main wash.

[0006] Conversely, there are situations where the product should have low viscosity. A low viscosity is desirable for easy dispensing of product from its bottle.

[0007] One weakness inherent in machine dishwashing gels as compared to dry product forms, such as powders and tablets, is poorer chemical stability of functional ingredients. Thus, the free water in gels can enhance both the decomposition of reactive molecules and any negative interactions between incompatible ingredients. This has not been a serious disadvantage in traditional gels based on chlorine bleach, phosphate builder and high pH because hypochlorite and phosphate are chemically compatible and hypochlorite-resistant structuring systems are available that give acceptable stability and viscosity profiles. However, incompatibility problems can lead to some deficiencies in gels. Thus, effective nonionic defoaming surfactants of the sort that are ubiquitous in powders have been difficult to incorporate into a gel because of poor compatibility with free hypochlorite.

[0008] Recently, there has been a trend in the marketplace towards lower pH, chlorine-free systems whose functionality is based on oxygen bleaching species and protease and amylase enzymes. This technology has first been incorporated into powders and tablets since physical or chemical stability problems are less significant in these product forms. However, there are a number of critical chemical stability problems in formulating a top performing machine dishwashing gel based on this oxygen bleach/enzyme technology. In particular, the stability of oxygen bleaching systems and retention of enzyme activity are both problematic in gels. Thus far, the only effective method of incorporating an effective oxygen bleach and enzymes in a machine dishwashing gel has been to encapsulate the bleach thereby physically separating it from the other ingredients. (See US-A-5,200,236.)

[0009] Formulations that contain oxygen bleach systems can lead to problems of tarnishing of silverware in the wash. Therefore, tarnish inhibitors such as benzotriazole and its derivatives are generally incorporated into machine dishwashing formulations containing oxygen bleaches in order to mitigate this negative effect. Again, tarnish inhibitors are more easily incorporated into a powder or a tablet product form than into a gel.

[0010] Whereas tarnish inhibitors can readily be incorporated into powders and tablets, problems often arise with gels or liquids. Thus, it was observed that although compositions containing an oxygen bleach and a tarnish inhibitor were functionally stable, the base formulations rapidly discolored during shelf storage and therefore were not pleasing to consumers.

Summary of the Invention

[0011] It was unexpectedly discovered that the addition of a relatively small amount of an inorganic compound, namely titanium dioxide, into a machine dishwashing gel composition containing an oxygen bleaching system, 10 to 50 wt. % of a builder material and an azole anti-tarnish agent provided a product which remained both functionally stable and color stable in storage. A method of processing such a gel formulation is also described.

[0012] The detergent builder is preferably either a monomeric carboxylate, a polymeric carboxylate or a mixture

thereof, or a mixture of phosphate salts (e.g. a tripolyphosphate or pyrophosphate). The oxygen bleach system is preferably a peracid or a peracid precursor with a source of hydrogen peroxide. The structuring system is preferably a high molecular weight cross-linked polycarboxylate, most preferably a cross-linked polyacrylate. The silver anti-tarnish agent is an aromatic azole, preferably a triazole.

Detailed Description of the Preferred Embodiments

Inorganic Stabilizing compound

[0013] An effective amount of an inorganic stabilizing compound such as titanium dioxide, prevents discoloration of machine dishwashing gel products as described herein. The combination of oxygen bleach and anti-tarnish agent can result in the generation of a highly colored species. Without being limited by theory, it is proposed that the inorganic compound either prevents the formation of this highly colored species, or limits its concentration to levels that do not result in discoloration of the gel.

[0014] The inorganic compound is present in an amount of from 0.0001 to 5 wt. % preferably 0.001 to 3 wt. %, most preferably 0.01 to 1 wt. %.

[0015] The gel compositions of the invention further comprise 10 to 50 wt. % of a builder, an effective amount of an oxygen bleach and an azole as described below.

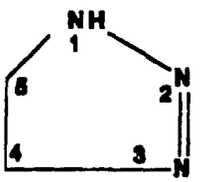
Silver Anti-Tarnish Agent

A. Azoles

[0016] Azoles useful as silver anti-tarnishing agents in the invention are nitrogen containing heterocylic 5-membered ring compounds which are present in a level of from 0.01% to 2.0% by weight, preferably from 0.01% to 0.5% by weight, most preferably from 0.02% to 0.1% by weight.

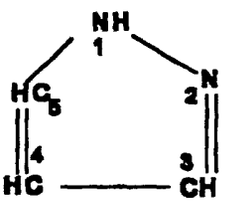
[0017] Such azoles include triazoles, pyrazoles, imidazoles, isoxazoles, oxazoles, isothiazoles, thiazoles and mixtures thereof as disclosed in US-A-2,618,608, US-A-2,742,369 and US-A-2,941,953.

[0018] The triazoles which can be employed in the composition of this invention are water-soluble 1,2,3-triazoles such as 1,2,3-triazole itself or a substituted 1,2,3-triazole where the substitution takes place in either the 4 or 5 position (or both) of the triazole ring as shown here by the structural formula:



[0019] Suitable triazoles include benzotriazole; tolyltriazole; 4-phenyl-1,2,3-triazole; 1,2-naphthotriazole and 4-nitrobenzotriazole; and the like, especially preferred is benzotriazole.

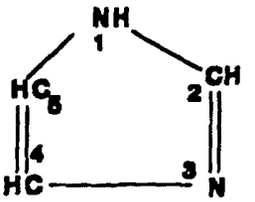
[0020] The pyrazoles which can be used in the composition of this invention include water-soluble pyrazoles such as pyrazole itself or a substituted pyrazole where the substitution takes place in the 3,4 or 5 position (or several of these positions) of the pyrazole ring as shown by the structural formula:



[0021] Suitable pyrazoles include pyrazole; 3,5-dimethyl pyrazole; 6-nitroindazole, 4-benzyl pyrazole; 4,5-dimethyl pyrazole; and 3-allyl pyrazole; and the like.

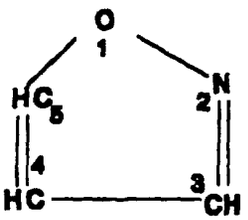
[0022] Imidazoles which can be used in the composition of this invention include water-soluble imidazoles such as

imidazole itself or a substituted imidazole where the substitution takes place in the 2,4 or 5 position (or several of these positions) of the imidazole ring as shown here by the structural formula:



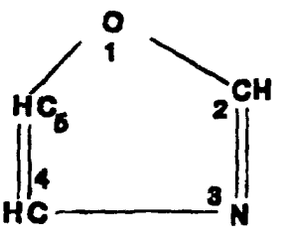
[0023] Suitable imidazoles which can be employed in the composition of this invention include imidazole; adenine; guanine; benzimidazole; 5-methyl benzimidazole; 2-phenyl imidazole; 2-benzyl imidazole; 4-allyl imidazole; 4-(betahydroxy ethyl)-imidazole; purine; 4-methyl imidazole; xanthine; hypoxanthine; 2-methyl imidazole; and the like.

[0024] Isoxazoles which can be employed in the composition of this invention include water-soluble isoxazoles such as isoxazole itself or a substituted isoxazole where the substitution takes place in the 3,4 or 5 position (or several of these positions) of the isoxazole ring as shown here by the structural formula:



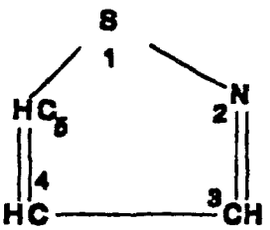
[0025] Suitable isoxazoles include isoxazole; 3-mercaptoisoxazole; 3-mercaptobenzisoxazole; benzisoxazole; and the like.

[0026] The oxazoles which can be employed in the composition of this invention include water-soluble oxazoles such as oxazole itself or a substituted oxazole where the substitution takes place in the 2,4 or 5 position (or several of these positions) of the oxazole ring as shown here by the structural formula:



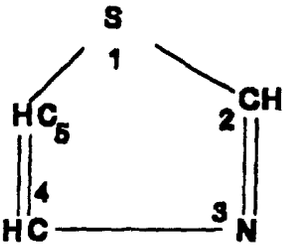
[0027] Suitable oxazoles include oxazole; 2-mercaptaxazole; 2-mercaptobenzoxazole; and the like.

[0028] The isothiazoles which can be employed in the compositions of this invention include water-soluble isothiazoles such as isothiazol itself or a substituted isothiazole where the substitution takes place in the 3, 4 or 5 position (or several of these positions) of the isothiazole ring as shown here by the structural formula:



[0029] Suitable isothiazoles include isothiazole; 3-mercaptoisothiazole; benzoisothiazole and the like.

[0030] The thiazoles which can be used in the composition of this invention include water-soluble thiazoles such as thiazole itself or a substituted thiazole where the substitution takes place in the 2, 4 or 5 position (or several of these positions) of the thiazole ring as shown here by the structural formula:

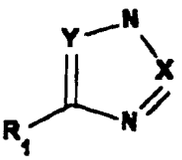


[0031] Suitable thiazoles include thiazole; 2-mercaptothiazole; 2-mercaptobenzothiazole; benzothiazole and the like.

[0032] In the above azole compounds, the constituents substituted in the azole rings can be alkyl, aryl, aralkyl, alkylol, and alkenyl radicals so long as the substituted azole is water soluble. Typically substituted members have from 1 to about 12 carbon atoms.

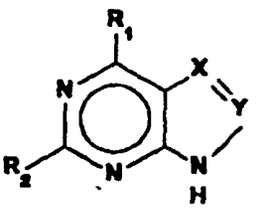
[0033] Specific 1,3 N-azoles which are useful include those azoles described in US-A-5,480,576 and US-A-5,468,410, herein incorporated by reference.

[0034] The 1,3 azole compounds have a formula:



wherein X is C-R_3 or X is nitrogen provided Y is also nitrogen, Y is nitrogen or C-R_2, and R_1, R_2 and R_3 are each independently a hydrogen, an amine, an amido, a straight or branched alkyl chain having from 1 to 20 carbon atoms, an amino or carboxylic containing chain, an alkoxy, an aklylthio, a hydroxy, a hydroxyalkyl and an alkenyl, or R_1 and R_2 taken together form a substituted or unsubstituted aryl; and salts corresponding thereto.

[0035] The purine compounds have a formula:



wherein X is nitrogen or C-R_3 and Y is nitrogen or C-R_4 and R_1, R_2, R_3 and R_4 are each independently a hydrogen, an oxygen, a hydroxy, an alkoxy, an amine, a straight or branched alkyl chain having 1 to 20 carbon atoms, an amido, an amidoaklyl, an alkylthio, an alkenyl or a hydroxalkyl.

[0036] Preferred azoles are the triazoles, particularly benzotriazole and the 1,3-N azoles, including the purines described above. Most preferred are the triazoles, especially benzotriazole.

Peroxy Bleaching Agents

[0037] The oxygen bleaching agents of the compositions include organic peroxy acids diacylperoxides, or mixtures thereof, inorganic peroxygen compounds and peracid precursors.

Peracids

[0038] Typical monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxy acids such as:

i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g., peroxy-alpha-naphthoic acid, and magnesium monoperoxyphthalate,

ii)aliphatic and substituted aliphatic monoperoxy acids, e.g., peroxylauric acid, peroxystearic acid, epsilon-phthalimido-peroxyhexanoic acid and o-carboxybenzamido peroxyhexanoic acid, N-nonylamidoperadipic acid and N-nonylamidopersuccinic acid, or mixtures of the last four,

iii)cationic peroxyacids such as those described in US-A-5,422,028, US-A-5,294,362; and US-A-5,292,447, U.S. Serial No. 08/738,504, Oakes et al.; and U.S. S/N 08/210,973, Oakes et al..

iv)Sulfonyl peroxyacids such as compounds described in US-A-5,039,447.

or mixtures of peroxybenzoic acid, aliphatic monoperoxy acids and substituted aliphatic monoperoxy acids.

[0039] Typical diperoxy acids useful herein include alkyl diperoxy acids and aryl diperoxy acids, such as:

v) 1,12-diperoxydodecanedioic acid
vi) 1,9-diperoxyazelaic acid
vii) diperoxybrassylic acid; diperoxysecacic acid and diperoxy-isophthalic acid
viii) 2-decyldiperoxybutan-1,4-dioic acid
ix) N,N^1-terephthaloyl-di(6-aminopercaproic acid).

[0040] Preferred peracid bleaching agents include epsilon-phthalimido-peroxyhexanoic acid, o-carboxybenzaminoperoxyhexanoic acid, and mixtures thereof. Also those peracids having a low solubility in water, such as N,N^1-terephthaloyl-di(6-aminopercaproic acid).

[0041] A typical diacylperoxide useful herein includes dibenzoylperoxide.

[0042] Inorganic peroxygen compounds are also suitable for the present invention. Examples of these materials useful in the invention are salts of monopersulfate, perborate monohydrate, perborate tetrahydrate, and percarbonate.

Bleach Precursors

[0043] Suitable peroxygen peracid precursors for peroxy bleach compounds have been amply described in the literature, including GB Nos. 836,988; 855,735; 907,356; 907;358; 907,950; 1,003,310 and 1,246,339; US-A-3,332,882 and US-A-4,128,494.

[0044] Typical examples of precursors are polyacylated alkylene diamines, such as N,N,N^1,N^1-tetraacetylethylene diamine (TAED) and N,N,N^1,N^1-tetraacetylmethylene diamine (TAMD); acylated glycolurils, such as tetraacetylglycoluril (TAGU); triacetylcyanurate, sodium sulfophenyl ethyl carbonic acid ester, sodium acetyloxybenene sulfonate (SABS), sodium nonanoyloxy benzene sulfonate (SNOBS) and choline sulfophenyl carbonate. Peroxybenzoic acid precursors are known in the art, e.g., as described in GB-A-836,988. Examples of suitable precursors are phenylbenzoate; phenyl p-nitrobenzoate; o-nitrophenyl benzoate; o-carboxyphenyl benzoate; p-bromophenylbenzoate; sodium or potassium benzoyloxy benzene-sulfonate; and benzoic anhydride.

[0045] Preferred peroxygen bleach precursors are sodium p-benzoyloxybenzene sulfonate, N,N,N^1,N^1-tetraacetylethylene diamine, sodium nonanoyloxybenzene sulfonate and choline sulfophenyl carbonate.

[0046] The oxygen bleaching agent is suitably present in the composition in an amount of from 1 to 20 weight percent, preferably 1 to 15 weight percent, most preferably 2 to 10 weight percent. The organic peroxy acid is present in the compositon in an amount such that the level of organic peroxy acid in the wash solution is 1 ppm to 100 ppm AvOx, most preferably 5 ppm to 30 ppm AvOx.

[0047] The oxygen bleaching agent may be incorporated directly into the formulation or may be encapsulated by any number of encapsulation techniques known in the art.

[0048] A preferred encapsulation method is described in US-A-5,200,236. In the patented method, the bleaching agent is encapsulated as a core in a paraffin wax material having a melting point from 40°C to 50°C. The wax coating has a thickness of from 100 to 1500 microns.

Detergent Builder Materials

[0049] The foregoing detergent builders are meant to illustrate but not limit the types of builders that can be employed in the present invention.

[0050] The compositions of this invention can contain all manner of detergent builders commonly taught for use in machine dishwashing or other cleaning compositions. The builders can include any of the conventional inorganic and organic water-soluble builder salts, or mixtures thereof and may comprise 1 to 75%, and preferably, from 5 to 70%, more preferably from 10 to 45% by weight of the cleaning composition.

[0051] Typical examples of phosphorus-containing inorganic builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates and polyphosphates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, pyrophosphates and hexametaphosphates.

[0052] Suitable examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, including layered silicates usch as SKS-6 ex. Hoechst, metasilicates, and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

[0053] Organic detergent builders can also be used in the present invention. Examples of organic builders include alkali metal citrates, succinates, malonates, fatty acid sulfonates, fatty acid carboxylates, nitrilotriacetates, phytates, phosphonates, alkanehydroxyphosphonates, oxydisuccinates, alkyl and alkenyl disuccinates, oxydiacetates, carboxymethyloxy succinates, ethylenediamine tetraacetates, tartrate monosuccinates, tartrate disuccinates, tartrate monoacetates, tartrate diacetates, oxidized starches, oxidized heteropolymeric polysaccharides, polyhydroxysulfonates, polycarboxylates such as polyacrylates, polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/polymaleate and polyacrylate/ polymethacrylate copolymers, acrylate/maleate/vinyl alcohol terpolymers, aminopolycarboxylates and polyacetal carboxylates, and polyaspartates and mixtures thereof. Such carboxylates are described in US-A-4,144,226, US-A-4,146,495 and US-A-4,686,062.

[0054] Alkali metal citrates, nitrilotriacetates, oxydisuccinates, polyphosphonates, acrylate/maleate copolymers and acrylate/maleate/vinyl alcohol terpolymers are especially preferred organic builders. When present they are preferably available from 5% to 70% of the total weight of the detergent compositions.

Sequestrants

[0055] The detergent compositions herein may also optionally contain one or more iron and/or manganese co-chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

[0056] Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraamine-hexaacetates, diethylenetriaminepentaacetates, ethylenediamine disuccinate, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

[0057] Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates), nitrilotris (methylenephosphonates) and diethylenetriaminepentakis (methylenephosphonates). Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

[0058] Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. (See US-A-3,812,044). Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

[0059] If utilized, these chelating agents will generally comprise from 0.1% to 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from 0.1% to 3.0% by weight of such composition.

Anti-Scalants

[0060] Scale formation on dishes and machine parts is an important problem that needs to be resolved or at least mitigated in formulating a machine warewashing product, especially in the case of low-phosphate (e.g. less than the equivalent of 20% by weight, particularly 10% by weight of sodium triphosphate) and phosphate-free machine warewashing compositions, particularly zero-P machine warewashing compositions.

[0061] In order to reduce this problem, co-builders, such as polyacrylic acids or polyacrylates (PAA), acrylate/maleate

copolymers, polyaspartates, ethylenediamine disuccinate and the various organic polyphosphonates, e.g. Dequest series, may be incorporated in one or more system components. For improved biodegradability, (as such co-builders), the block co-polymers of formula (I) as defined in published PCT patent specification WO 94/17170 may also be used. In any component, the amount of anti-scalant may be in the range of from 0.5 to 10, preferably from 0.5 to 5, and more preferably from 1 to 5% by weight.

Surfactants

[0062] A surfactant may be included in the first layer including anionic, nonionic, cationic, amphoteric, zwitteronic surfactants and mixtures of these surface active agents. Such surfactants are well known in the detergent arts and are described at length in "Surface Active Agents and Detergents", Vol. 2 by Schwartz, Perry and Birch, Interscience Publishers, Inc., 1959, herein incorporated by reference.

[0063] Preferred surfactants are one or a mixture of:

Anionic surfactants

[0064] Anionic synthetic detergents can be broadly described as surface active compounds with one or more negatively charged functional groups. An important class of anionic compounds are the water-soluble salts, particularly the alkali metal salts, of organic sulfur reaction products having in their molecular structure an alkyl radical containing from about 6 to 24 carbon atoms and a radical selected from the group consisting of sulfonic and sulfuric acid ester radicals.

Primary Alkyl Sulfates

[0065]

$$R^1OSO_3M$$

where R^1 is a primary alkyl group of 8 to 18 carbon atoms and M is a solubilizing cation. The alkyl group R^1 may have a mixture of chain lengths. It is preferred that at least two thirds of the R^1 alkyl groups have a chain length of 8 to 14 carbon atoms. This will be the case if R^1 is coconut alkyl, for example. The solubilizing cation may be a range of cations which are in general monovalent and confer water solubility. Alkali metal, notably sodium, is especially envisaged. Other possibilities are ammonium and substituted ammonium ions, such as trialkanolammonium or trialkylammonium.

Alkyl Ether Sulfates

[0066]

$$R^1O(CH_2CH_2O)_nSO_3M$$

where R^1 is a primary alkyl group of 8 to 18 carbon atoms, n has an average value in the range from 1 to 6 and M is a solubilizing cation. The alkyl group R^1 may have a mixture of chain lengths. It is preferred that at least two thirds of the R^1 alkyl groups have a chain length of 8 to 14 carbon atoms. This will be the case if R^1 is coconut alkyl, for example. Preferably n has an average value of 2 to 5.

Fatty *Acid Ester Sulfonates*

[0067]

$$R^2CH\ (SO_3M)\ CO_2R^3$$

where R^2 is an alkyl group of 6 to 16 atoms, R^3 is an alkyl group of 1 to 4 carbon atoms and M is a solubilizing cation. The group R^2 may have a mixture of chain lengths. Preferably at least two thirds of these groups have 6 to 12 carbon atoms. This will be the case when the moiety $R^2CH(-)CO_2(-)$ is derived from a coconut source, for instance. It is preferred that R^3 is a straight chain alkyl, notably methyl or ethyl.

Alkyl Benzene Sulfonates

[0068]

$$R^4ArSO_3M$$

where R^4 is an alkyl group of 8 to 18 carbon atoms, *Ar* is a benzene ring (C_6H_4) and M is a solubilizing cation. The group R^4 may be a mixture of chain lengths. Straight chains of 11 to 14 carbon atoms are preferred.

[0069] *Organic phosphate* based anionic surfactants include organic phosphate esters such as complex mono- or diester phosphates of hydroxyl- terminated alkoxide condensates, or salts thereof. Included in the organic phosphate esters are phosphate ester derivatives of polyoxyalkylated alkylaryl phosphate esters, of ethoxylated linear alcohols and ethoxylates of phenol. Also included are nonionic alkoxylates having a sodium alkylenecarboxylate moiety linked to a terminal hydroxyl group of the nonionic through an ether bond. Counterions to the salts of all the foregoing may be those of alkali metal, alkaline earth metal, ammonium, alkanolammonium and alkylammonium types.

[0070] *Paraffin sulfonates* having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, in the alkyl moiety. These surfactants are commercially available at Hostapur SAS from *Hoechst Celanese*.

[0071] *Olefin sulfonates* having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms. U.S. Patent No. 3,332,880 contains a description of suitable olefin sulfonates.

[0072] Particularly preferred anionic surfactants are the fatty acid ester sulfonates with formula:

$$R^2CH(SO_3M)CO_2R^3$$

where the moiety $R^2CH(-)CO_2(-)$ is derived from a coconut source and R^3 is either methyl or ethyl; primary alkyl sulfates with the formula:

$$R^1OSO_3M$$

wherein R^1 is a primary alkyl group of 10 to 18 carbon atoms and M is a sodium cation; and paraffin sulfonates, preferably with 12 to 16 carbon atoms to the alkyl moiety.

Nonionic surfactants

[0073] Nonionic surfactants can be broadly defined as surface active compounds with one or more uncharged hydrophilic substituents. A major class of nonionic surfactants are those compounds produced by the condensation of alkylene oxide groups with an organic hydrophobic material which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Illustrative, but not limiting examples, of various suitable nonionic surfactant types are:

polyoxyalkene condensates of aliphatic carboxylic acids, whether linear- or branched-chain and unsaturated or saturated, especially ethoxylated and/or propoxylated aliphatic alcohols containing from about 8 to about 18 carbon atoms in the aliphatic chain and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable carboxylic acids include "coconut" fatty acids (derived from coconut oil) which contain an average of about 12 carbon atoms, "tallow" fatty acids (derived from tallow-class fats) which contain an average of about 18 carbon atoms, palmitic acid, myristic acid, stearic acid and lauric acid,

polyoxyethylene or polyoxypropylene condensates of aliphatic alcohols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to about 24 carbon atoms and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable alcohols include "coconut" fatty alcohol, "tallow" fatty alcohol, lauryl alcohol, myristyl alcohol and oleyl alcohol.

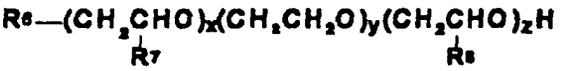
[0074] Ethoxylated fatty alcohols may be used alone or in admixture with anionic surfactants, especially the preferred surfactants above. The average chain lengths of the alkyl group R^5 in the general formula:

$$R^5O(CH_2CH_2O)_nH$$

is from 6 to 20 carbon atoms. Notably the group R^5 may have chain lengths in a range from 9 to 18 carbon atoms.

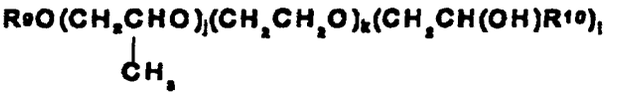
[0075] The average value of *n* should be at least 2. The numbers of ethylene oxide residues may be a statistical distribution around the average value. However, as is known, the distribution can be affected by the manufacturing process or altered by fractionation after ethoxylation. Particularly preferred ethoxylated fatty alcohols have a group R^5 which has 9 to 18 carbon atoms while *n* is from 2 to 8.

[0076] Also included within this category are nonionic surfactants having a formula:



wherein R^6 is a linear alkyl hydrocarbon radical having an average of 6 to 18 carbon atoms, R^7 and R^8 are each linear alkyl hydrocarbons of about 1 to about 4 carbon atoms, x is an integer of from 1 to 6, y is an integer of from 4 to 20 and z is an integer from 4 to 25.

[0077] One preferred nonionic surfactant of the above formula is Poly-Tergent SLF-18[7] a registered trademark of the Olin Corporation, New Haven, Conn. having a composition of the above formula where R^6 is a C_6-C_{10} linear alkyl mixture, R^7 and R^8 are methyl, x averages 3, y averages 12 and z averages 16. Another preferred nonionic surfactant is



wherein R^9 is a linear, aliphatic hydrocarbon radical having from about 4 to about 18 carbon atoms including mixtures thereof; and R^{10} is a linear, aliphatic hydrocarbon radical having from about 2 to about 26 carbon atoms including mixtures thereof; j is an integer having a value of from 1 to about 3; k is an integer having a value from 5 to about 30; and z is an integer having a value of from 1 to about 3. Most preferred are compositons in which j is 1, k is from about 10 to about 20 and l is 1. These surfactants are described in WO 94/22800. Other preferred nonionic surfactants are linear fatty alcohol alkoxylates with a capped terminal group, as described in US-A-4,340,766. Particularly preferred is Plurafac LF403 ex. BASF.

[0078] Another nonionic surfactant included within this category are compounds of formula:

$$R^{11}\text{-}(CH_2CH_2O)_qH$$

wherein R^{11} is a C_6-C_{24} linear or branched alkyl hydrocarbon radical and q is a number from 2 to 50; more preferably R^{11} is a C_8-C_{18} linear alkyl mixture and q is a number from 2 to 15.

[0079] *polyoxyethylene or polyoxypropylene condensates of alkyl phenols*, whether linear- or branched-chain and unsaturated or saturated,containing from about 6 to 12 carbon atoms and incorporating from about 2 to about 25 moles of ethylene oxide and/or propylene oxide.

[0080] *polyoxyethylene derivatives of sorbi tan mono-, di- , and tri-fatty acid esters* wherein the fatty acid component has between 12 and 24 carbon atoms. The preferred polyoxyethylene derivatives are of sorbitan monolaurate, sorbitan trilaurate, sorbitan monopalmitate, sorbitan tripalmitate, sorbitan monostearate, sorbitan monoisostearate, sorbitan tripalmitate, sorbital tristearate, sorbitan monooleate, and sorbitan trioleate. The polyoxyethylene chains may contain between about 4 and 30 ethylene oxide units, preferably about 10 to 20. The sorbitan ester derivatives contain 1, 2 or 3 polyoxyethylene chains dependent upon whether they are mono-, di- or tri-acid esters.

[0081] *polyoxyethylene-polyoxypropylene block copolymers* having formula:

$$HO(CH_2CH_2O)_a(CH(CH_3)\ CH_2O)_b(CH_2CH_2O)_cH$$

or

$$HO(CH(CH_3)CH_2O)_d(CH_2CH_2O)_e(CH(CH_3)CH_2O)_fH$$

wherein a, b, c, d, e and f are integers from 1 to 350 reflecting the respective polyethylene oxide and polypropylene oxide blocks of said polymer. The polyoxyethylene component of the block polymer constitutes at least about 10% of the block polymer. The material preferably has a molecular weight of between about 1,000 and 15,000, more preferably from about 1,500 to about 6,000. These materials are well-known in the art. They are available under the trademark "Pluronic" and "Pluronic R", a product of BASF Corporation.

[0082] *Amine oxides* having formula:

$$R^{12}R^{13}R^{14}N{=}O$$

wherein R^{12}, R^{13} and R^{14} are saturated aliphatic radicals or substituted saturated aliphatic radicals. Preferable amine oxides are those wherein R^{12} is an alkyl chain of about 10 to about 20 carbon atoms and R^{13} and R^{14} are methyl or ethyl groups or both R^{12} and R^{13} are alkyl chains of about 6 to about 14 carbon atoms and R^{14} is a methyl or ethyl group.

[0083] *Amphoteric* synthetic detergents can be broadly described as derivatives of aliphatic tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contain from about 8 to about 18 carbons and one contains an anionic water-solubilizing group, i.e., carboxy, sulpho, sulphato, phosphato or phosphono. Examples of compounds falling within this definition are sodium 3-dodecylamino propionate and sodium 2-dodecylamino propane sulfonate.

[0084] *Zwitterionic* synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium and sulphonium compounds in which the aliphatic radical may be straight chained or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulpho, sulphato, phosphato or phosphono. These compounds are frequently referred to as betaines. Besides alkyl betaines, alkyl amino and alkyl amido betaines are encompassed within this invention.

Alkyl Glycosides

[0085]

$$R^{15}O(R^{16}O)_n(Z^1)_p$$

wherein R^{15} is a monovalent organic radical (e.g., a monovalent saturated aliphatic, unsaturated aliphatic or aromatic radical such as alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl, aryl, alkylaryl, hydroxyalkylaryl, arylalkyl, alkenylaryl, arylalkenyl, etc.) containing from about 6 to about 30 (preferably from about 8 to 18 and more preferably from about 9 to about. 13) carbon atoms; R^{16} is a divalent hydrocarbon radical containing from 2 to about 4 carbon atoms such as ethylene, propylene or butylene (most preferably the unit $(R^{16}O)_n$ represents repeating units of ethylene oxide, propylene oxide and/or random or block combinations thereof); n is a number having an average value of from 0 to about 12; Z^1 represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms (most preferably a glucose unit); and p is a number having an average value of from 0.5 to about 10 preferably from about 0.5 to about 5 .

[0086] Examples of commercially available materials from Henkel Kommanditgesellschaft Aktien of Dusseldorf, Germany include APG^7 300, 325 and 350 with R^{15} being C_9-C_{11}, n is 0 and p is 1.3, 1.6 and 1.8-2.2 respectively; APG^7 500 and 550 with R^{15} is C_{12}-C_{13}, n is 0 and p is 1.3 and 1.8-2.2, respectively; and APG^7 600 with R^{15} being C_{12}-C_{14}, n is 0 and p is 1.3.

[0087] While esters of glucose are contemplated especially, it is envisaged that corresponding materials based on other reducing sugars, such as galactose and mannose are also suitable.

[0088] The preferred range of surfactant is from 0.5 to 30 % by wt., more preferably from 0.5 to 15% by wt of the composition.

Filler

[0089] An inert filler material which is water-soluble may also be present in the machine dishwashing compositions. This material should not precipitate calcium or magnesium ions at the filler use level. Suitable for this purpose are organic or inorganic compounds. Organic fillers include sucrose esters and urea. Representative inorganic fillers include sodium sulfate, sodium chloride and potassium chloride. A preferred filler is sodium sulfate. Its concentration

may range from 0% to 20%, preferably from 2% to 10% by weight of the cleaning composition.

Thickening Agents

[0090] Thickeners are often desirable for liquid cleaning compositions. Thixotropic thickeners such as smectite clays including montmorillonite (bentonite), hectorite, saponite, and the like may be used to impart viscosity to liquid cleaning compositions. Silica, silica gel, and aluminosilicate may also be used as thickeners. Use of clay thickeners for machine dishwashing compositions is disclosed for example in US-A-4,431,559; US-A-4,511,487; US-A-4,740,327; US-A-4,752,409. Commercially available synthetic smectite clays include Laponite supplied by Laporte Industries. Commercially available bentonite clays include Korthix H and VWH ex Combustion Engineering, Inc.; Polargel T ex American Colloid Co.; and Gelwhite clays (particularly Gelwhite GP and H) ex English China Clay Co. Polargel T is preferred as imparting a more intense white appearance to the composition than other clays. The amount of clay thickener employed in the compositions is from 0.1 to 10%, preferably 0.5 to 5%.

[0091] The amount of thickener employed in the compositions is from 0 to 5%, preferably 0.5-3%.

[0092] One type of agent useful in the gel composition of the invention is a cross-linked polycarboxylate, preferably a polyacrylate acrylic acid polymer. Particularly preferred are salts of polyacrylic acid of molecular weight of from 300,000 up to 6 million and higher which are cross-linked.

[0093] Acrylic acid polymers that are cross-linked manufactured by, for example, B.F. Goodrich and sold under the trade name "Carbopol" or by 3V Inc. and sold under the tradename Polygel DA have been found to be effective for production of the inventive formulas. Carbopol 940, 610, 617 and 627, having a molecular weight of 4,000,000, are particularly preferred.

[0094] Polymeric carboxylic acids described in GB 2,164,350A; US-A-4,859,358 and US-A-4,836,948 are also useful in the invention and are incorporated by reference.

[0095] Conventional stabilizers such as long-chain calcium and sodium soaps and C_{12} to C_{18} sulfates are detailed in US-A-3,956,158 and US-A-4,271,030 and the use of other metal salts of long-chain soaps is detailed in US-A-4,752,409. Other stabilizers include Laponite and metal oxides and their salts as described in US-A-4,933,101. The amount of stabilizer which may be used in the liquid cleaning compositions is from 0.01 to 5% by weight of the composition, preferably 0.01-2%. Such stabilizers are optional in gel formulations. Stabilizers which are found especially suitable for gels include trivalent metal ions at 0.01-4% of the compositions, Laponite and/or water-soluble structuring chelants at 0.01-5%. These stabilizers are more fully described in US-A-5,141,664.

Defoamer

[0096] The formulations of the cleaning composition comprising surfactant may further include a defoamer. Suitable defoamers include mono-and distearyl acid phosphate, silicone oil and mineral oil. Even if the cleaning composition has only defoaming surfactant, the defoamer assists to minimize foam which food soils can generate. The compositions may include 0.02 to 2% by weight of defoamer, or preferably 0.05-1.0%.

Enzymes

[0097] Enzymes capable of facilitating the removal of soils from a substrate may also be present in an amount of up to about 10% by wt., preferably 1 to about 5 wt. %. Such enzymes include proteases (e.g., Alcalase7, Savinase7 and Esperase7 from Novo Industries A/S and Purafect OxP, ex. Genencor), amylases (e.g., Termamyl7 and Duramyl7 from Novo Industries and Purafect OxAm, ex. Genencor) and lipases (e.g. Lipolase7 from Novo Industries).

Optional Ingredients

[0098] Minor amounts of various other components may be present in the cleaning composition. These include bleach scavengers including but not limited to sodium bisulfite, sodium perborate, reducing sugars, and short chain alcohols; solvents and hydrotropes such as ethanol, isopropanol and xylene sulfonates; enzyme stabilizing agents; soil suspending agents; antiredeposition agents; anti-corrosion agents, such as isocyanuric acid described in US-A-5,374,369; ingredients to enhance decor care such as certain aluminum salts described in U.S. Serial No. 08/444,502 and 08/444,503; and anti-foaming agents such as those described in U.S. Serial No. 08/540,285 and 08/539,923; colorants; perfumes; and other functional additives.

[0099] The following example will serve to distinguish this invention from the prior art and illustrate its embodiments more fully. Unless otherwise indicated, all parts, percentages and proportions referred to are by weights.

Example 1

[0100] The following inventive gel composition was prepared:

Table 1

Ingredient	Sample A % by Weight
Citrate	30.0
Sokalan CP7[1]	5.0
TiO_2	0.1
Sulfite	0.1
Carbopol 627[2]	1.5
Glycerol	6.0
Sodium Tetraborate	3.0
Enzymes	1.2
Plurafac LF 403[3]	2.0
PAP[4]	4.0
BTA[5]	0.05
NaOH	0.8
Water	to 100%

[1] an acrylate/maleate copolymer from BASF

[2] a high molecular weight cross-linked polyacrylate structurant from B.F. Goodrich.

[3] nonionic surfactant supplied by BASF.

[4] encapsulated by the method described in U.S.-A-5,200,236.

[5] incorporated via dissolution in the surfactant.

[0101] The composition contains the peracid, phthalimidoperhexanoic acid (PAP), encapsulated in wax and the pH of the gel is 8.5. BTA was incorporated via pre-dissolution in the Plurafac nonionic surfactant. The TiO_2 (0.1%) was incorporated into the base liquid.

[0102] A second composition (B) was also prepared except the TiO_2 was not incorporated. These two formulations were stored at ambient temperature and at 45°C for at least 14 weeks.

[0103] After 14 weeks storage at ambient temperature Sample A, within the scope of the invention, showed no visible change from its original white color. Sample (B), however, showed a considerable degree of yellow discoloration within the gel.

[0104] The melting point of the wax used to coat the PAP peracid lies in the range 42-46°C. Therefore, storage at a temperature of 45°C represents an extreme test condition designed to cause early melting of the wax coating and full release of the peracid into the gel. After two days the gel of Sample (B) was very intensely yellow-colored. In contrast, there was a barely perceptible color change observed in Sample (A), containing the TiO_2.

Example 2

[0105] The following inventive Sample (C) was prepared.

Ingredient	% by Weight-Sample C
Water	to 100
Carbopol 627	1.5
Sodium Citrate	30.0
Sorbitol	6.0
Borax	3.0

(continued)

Ingredient	% by Weight-Sample C
Sokalan CP-7	5.0
Plurafac LF 403	2.0
Suspended TPCAP	1.7
BTA	0.05
TiO_2	0.1

[0106] In Sample C the peracid [N,N'-terephthaloyl-di(-6-amino percaproic acid)] (TPCAP) was suspended in the gel and the pH of the gel is 6.5

[0107] A second Sample D was prepared, which was identical to Sample C except for the fact that TiO_2 was not incorporated into the base liquid. These two formulations were stored at 40°C as described in Example 1.

[0108] After one week at 40°C there was no visible discoloration of Sample C containing TiO_2. Sample D showed a distinctive yellow discoloration.

Titanium dioxide preserved the white appearance of the product even when both the peracid and BTA were suspended "free" within the gel formulation.

Claims

1. A detergent gel composition for machine dishwashing comprising:

(a)1 to 75% by wt. of a builder material;
(b)an effective amount of an oxygen bleaching agent;
(c)0.01 to 2.0% by weight of an azole compound; and
(d) 0.0001 to 5 wt. % of an inorganic stabilizing compound selected from the group consisting of titanium dioxide.

2. A detergent composition according to claim 1, wherein the builder material is an organic compound selected from the group of a monomeric carboxylate, polymeric carboxylate and mixtures thereof.

3. A detergent composition according to claim 2, wherein the builder is present in an amount of 10 to 45 wt. %.

4. A detergent composition according to claim 1, wherein the azole is a triazole azole.

5. A detergent composition according to claim 4, wherein the trizazole is benzotriazole.

6. A detergent composition according to claim 1, wherein the oxygen bleaching agent is present in an amount of from 1 to 20 wt. %.

7. A detergent composition according to claim 1, wherein the oxygen bleaching agent is selected from the group of organic peroxy acids, diacylperoxides and mixtures thereof.

8. A detergent composition according to claim 7, wherein the organic peroxy acids are selected from the group consisting of peroxybenzoic acid, aliphatic monoperoxy acids, substituted aliphatic monoperoxy acids and mixtures thereof.

9. A detergent composition according to claim 8, wherein the substituted aliphatic monoperoxy acids are selected from the group consisting of epsilon-phthalimidoperoxyhexanoic acid, o-carboxybenzamido peroxyhexanoic acid, N-nonylamidoperadipic acid, N-nonylamidopersuccinic acid and mixtures thereof.

10. A detergent composition according to claim 7, wherein the oxygen bleaching agent is wax encapsulated.

11. A detergent composition according to claim 1, wherein the composition further comprises an effective amount of

an enzyme.

12. A detergent composition according to claim 1, further comprising 0.5 to 30 wt. % of a surfactant.

13. A detergent composition according to claim 1, wherein the builder material is an inorganic builder.

14. A detergent composition according to claim 13, wherein the inorganic builder is a phosphorus containing compound selected from the group consisting of alkali metal pyrophosphates, orthophosphates, polyphosphates and mixtures thereof.

15. A detergent compositon according to claim 13, wherein the inorganic builder is a non-phosphorus containing builder selected from the group consisting of alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, metasilicates, crystalline aluminosilicates, amorphous aluminosilicates and mixtures thereof.

16. A method of cleaning dishware in a machine dishwasher comprising the steps of:

1. applying a dishwashing composition onto dishware in a machine dishwasher, said composition comprising:

(a) 1 to 75% by wt. of a builder material,
(b) an effective amount of an oxygen bleaching agent,
(c) 0.01 to 2.0% by weight of an azole compound, and
(d) 0.001 to 5 wt. % of an inorganic stabilizing compound selected from the group consisting of titanium dioxide, and

2. substantially cleaning the dishware in the dishwasher.

Patentansprüche

1. Waschmittelgelzusammensetzung zum Maschinengeschirrspülen, umfassend:

(a) 1-75 Gew.-% eines Buildermaterials;
(b) eine wirksame Menge eines Sauerstoffbleichmittels;
(c) 0,01 bis 2,0 Gew.-% einer Azolverbindung; und
(d) 0,0001 bis 5 Gew.-% einer anorganischen, stabilisierenden Verbindung, ausgewählt aus der Gruppe, bestehend aus Titandioxid.

2. Waschmittelzusammensetzung nach Anspruch 1, worin das Buildermaterial eine organische Verbindung, ausgewählt aus der Gruppe von einem monomeren Carboxylat, polymeren Carboxylat und Gemischen davon, darstellt.

3. Waschmittelzusammensetzung nach Anspruch 2, worin der Builder in einer Menge von 10 bis 45 Gew.-% vorliegt.

4. Waschmittelzusammensetzung nach Anspruch 1, worin das Azol ein Triazol-Azol darstellt.

5. Waschmittelzusammensetzung nach Anspruch 4, worin das Triazol Benzotriazol darstellt.

6. Waschmittelzusammensetzung nach Anspruch 1, worin das Sauerstoffbleichmittel in einer Menge von 1 bis 20 Gew.-% vorliegt.

7. Waschmittelzusammensetzung nach Anspruch 1, worin das Sauerstoffbleichmittel aus der Gruppe von organischen Peroxysäuren, Diacylperoxiden und Gemischen davon ausgewählt ist.

8. Waschmittelzusammensetzung nach Anspruch 7, worin die organischen Peroxysäuren aus der Gruppe, bestehend aus Peroxybenzoesäure, aliphatischen Monoperoxysäuren, substituierten aliphatischen Monoperoxysäuren und Gemischen davon, ausgewählt sind.

9. Waschmittelzusammensetzung nach Anspruch 8, worin die substituierten aliphatischen Monoperoxysäuren aus der Gruppe, bestehend aus ε-Phthalimidoperoxyhexansäure, o-Carboxybezamidoperoxyhexansäure, N-Nonyl-

amidoperadipinsäure, N-Nonylamidoperbernsteinsäure und Gemischen davon, ausgewählt sind.

10. Waschmittelzusammensetzung nach Anspruch 7, worin das Sauerstoffbleichmittel in Wachs eingekapselt ist.

11. Waschmittelzusammensetzung nach Anspruch 1, worin die Zusammensetzung weiterhin eine wirksame Menge eines Enzyms umfasst.

12. Waschmittelzusammensetzung nach Anspruch 1, die weiterhin 0,5 bis 30 Gew.-% eines Tensids umfasst.

13. Waschmittelzusammensetzung nach Anspruch 1, worin das Buildermaterial ein anorganischer Builder ist.

14. Waschmittelzusammensetzung nach Anspruch 13, worin der anorganische Builder eine phosphorenthaltende Verbindung ist, ausgewählt aus der Gruppe, bestehend aus Alkalimetallpyrophosphaten, -orthophosphaten, -polyphosphaten und Gemischen davon.

15. Waschmittelzusammensetzung nach Anspruch 13, worin der anorganische Builder ein nichtphosphorenthaltender Builder ist, ausgewählt aus der Gruppe, bestehend aus Alkalimetallcarbonaten, -bicarbonaten, -sesquicarbonaten, -boraten, -silikaten, -metasilikaten, kristallinen Aluminosilikaten, amorphen Aluminosilikaten und Gemischen davon.

16. Verfahren zum Reinigen von Geschirr in einem Maschinengeschirrspüler, umfassend die Schritte von:

1. Anwenden einer Geschirrspülzusammensetzung auf Geschirr in einem Maschinengeschirrspüler, wobei die Zusammensetzung umfasst:

(a) 1 bis 75 Gew.-% eines Buildermaterials,
(b) eine wirksame Menge eines Sauerstoffbleichmittels,
(c) 0,01 bis 2,0 Gew.-% einer Azolverbindung und
(d) 0,001 bis 5,0 Gew.-% einer anorganischen, stabilisierenden Verbindung, ausgewählt aus der Gruppe, bestehend aus Titandioxid und

2. im Wesentlichen Reinigen des Geschirrs in dem Geschirrspüler.

Revendications

1. Composition de gel détergent pour machine à laver la vaisselle comprenant :

(a) 1 à 75 % en poids d'un matériau adjuvant ;
(b) une quantité efficace d'un agent de blanchiment oxygéné ;
(c) 0,01 à 2% en poids d'un composé azole ; et
(d) 0,0001 à 5% en poids d'un composé inorganique stabilisant choisi dans le groupe constitué du dioxyde de titane.

2. Composition de détergent selon la revendication 1, dans laquelle le matériau adjuvant est un composé organique choisi dans le groupe constitué par un carboxylate monomère, un carboxylate polymère et leur mélange.

3. Composition de détergent selon la revendication 2, dans laquelle l'adjuvant est présent dans une quantité de 10 à 45% en poids.

4. Composition de détergent selon la revendication 1, dans laquelle l'azole est un azole triazole.

5. Composition de détergent selon la revendication 4, dans laquelle le triazole est du benzotriazole.

6. Composition de détergent selon la revendication 1, dans laquelle l'agent de blanchiment oxygéné est présent dans une quantité de 1 à 20% en poids.

7. Composition de détergent selon la revendication 1, dans laquelle l'agent de blanchiment oxygéné est choisi dans

le groupe des acides peroxycarboxyliques organiques, des diacylperoxydes et de leur mélange.

8. Composition de détergent selon la revendication 7, dans laquelle les acides peroxycarboxyliques organiques sont choisis dans le groupe constitué par l'acide peroxybenzoïque, les acides monoperoxycarboxyliques aliphatiques et les acides monoperoxycarboxyliques substitués et leur mélange.

9. Composition de détergent selon la revendication 8, dans laquelle les acides monoperoxycarboxyliques aliphatiques substitués sont choisis dans le groupe constitué par l'acide epsilon-phtalimidoperoxyhexanoïque, l'acide o-carboxybenzamidoperoxyhexanoïque, l'acide N-nonylamidoperadipique, l'acide N-nonylamidopersuccinique et leur mélange.

10. Composition de détergent selon la revendication 7, dans laquelle l'agent de blanchiment oxygéné est de la cire capsulée.

11. Composition de détergent selon la revendication 1, dans laquelle la composition comprend en outre une quantité efficace d'un enzyme.

12. Composition de détergent selon la revendication 1, comprenant en outre 0,5 à 30% en poids d'un surfactant.

13. Composition de détergent selon la revendication 1, dans laquelle le matériau adjuvant est un adjuvant inorganique.

14. Composition de détergent selon la revendication 13, dans laquelle l'adjuvant inorganique est un composé contenant du phosphore choisi dans le groupe constitué par les pyrophosphates, les orthophosphates, les polyphosphates de métaux alcalins et leur mélange.

15. Composition de détergent selon la revendication 13, dans laquelle l'adjuvant inorganique est un adjuvant ne contenant pas du phosphore choisi dans le groupe constitué par les carbonates, les bicarbonates, les sesquicarbonates, les borates, les silicates, les métasilicates, les aluminosilicates cristallins, les aluminosilicates amorphes de métaux alcalins et leur mélange.

16. Procédé de lavage de vaisselle dans une machine à laver la vaisselle comprenant les étapes consistant à :

1. appliquer une composition de produit vaisselle sur la vaisselle dans un lave-vaisselle, ladite composition comprenant :

(a) 1 à 75% en poids d'un matériau adjuvant,
(b) une quantité efficace d'un agent de blanchiment oxygéné.
(c) 0,01 à 2,0% en poids d'un composé azole, et
(d) 0,001 à 5% en poids d'un composé inorganique stabilisant choisi dans le groupe constitué du dioxyde de titane, et

2. laver essentiellement la vaisselle dans le lave-vaisselle.