

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 846 757 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
10.06.1998 Bulletin 1998/24

(51) Int. Cl.⁶: **C11D 17/00**, C11D 3/39,
C11D 3/28, C11D 3/12

(21) Application number: **97203470.6**

(22) Date of filing: **11.11.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **05.12.1996 US 760850**

(71) Applicants:
• **UNILEVER N.V.**
3000 DK Rotterdam (NL)
Designated Contracting States:
BE CH DE DK ES FI FR GR IT LI LU NL PT SE AT

• **UNILEVER PLC**
London EC4P 4BQ (GB)
Designated Contracting States:
GB IE

(72) Inventors:
• **Nicholson, John Richard**
Edgewater, NJ 07020 (US)
• **Piatek, Bozena Marianna**
Edgewater, NJ 07020 (US)

(74) Representative:
Tansley, Sally Elizabeth et al
Unilever PLC,
Patent Division,
Colworth House
Sharbrook, Bedford MK44 1LQ (GB)

(54) **Machine dishwashing gel composition**

(57) A detergent gel composition which both delivers high performance cleaning and does not discolor in storage is described. The composition contains 0.001 wt. % to 5 wt. % of an inorganic compound such as titanium dioxide, 1 to 75% by wt. of a builder material, an effective amount of an oxygen bleaching agent, and 0.01 to 2.0% by weight of an azole compound.

EP 0 846 757 A2

Description**Field of the Invention**

5 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

10 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.

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

 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.

20 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.

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

 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.

35 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.)

40 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.

45 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

55 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.

 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

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.

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. %.

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.

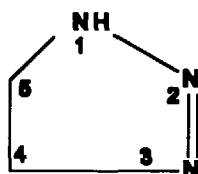
Silver Anti-Tarnish Agent

A. Azoles

Azoles useful as silver anti-tarnishing agents in the invention are nitrogen containing heterocyclic 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.

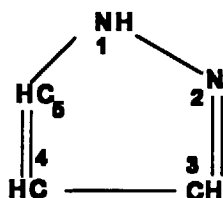
Such azoles include triazoles, pyrazoles, imidazoles, isoxazoles, oxazoles, isothiazoles, thiazoles and mixtures thereof as disclosed in US-A-2,618,608, US-A-2,742,369 and US-A-2,941,953.

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:



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

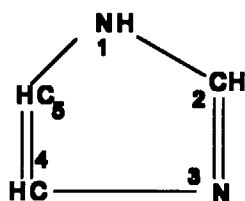
The pyrazoles which can be used in the composition of this invention include water-soluble pyrazoles such as pyrazole itself or a substituted pyrazole where the substitution takes place in the 3,4 or 5 position (or several of these positions) of the pyrazole ring as shown by the structural formula:



Suitable pyrazoles include pyrazole; 3,5-dimethyl pyrazole; 6-nitroindazole, 4-benzyl pyrazole; 4,5-dimethyl pyra-

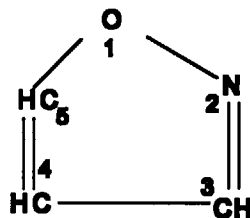
zole; and 3-allyl pyrazole; and the like.

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:



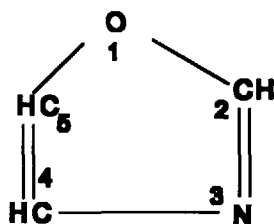
Suitable imidazoles which can be employed in the composition of this invention include imidazole; adenine; guanine; benzimidazole; 5-methyl benzimidazole; 2-phenyl imidazole; 2-benzyl imidazole; 4-allyl imidazole; 4-(beta-hydroxy ethyl)-imidazole; purine; 4-methyl imidazole; xanthine; hypoxanthine; 2-methyl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

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:



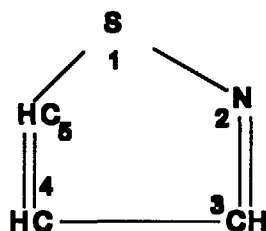
Suitable isoxazoles include isoxazole; 3-mercaptoisoxazole; 3-mercaptobenzisoxazole; benzisoxazole; and the like.

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:



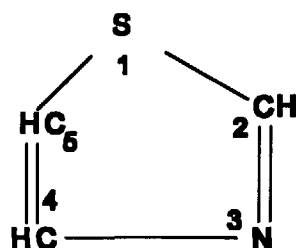
Suitable oxazoles include oxazole; 2-mercaptaxazole; 2-mercaptobenzoxazole; and the like.

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:



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

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:

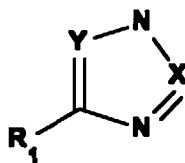


Suitable thiazoles include thiazole; 2-mercaptothiazole; 2-mercaptobenzothiazole; benzothiazole and the like.

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.

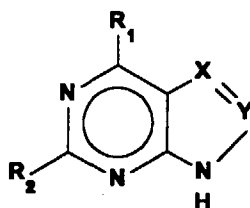
Specific 1,3 N-azoles which are useful include those azoles described in US-A-5,480,576 and US-A-5,468,410, herein incorporated by reference.

The 1,3 azole compounds have a formula:



wherein X is C-R₃ or X is nitrogen provided Y is also nitrogen, Y is nitrogen or C-R₂, and R₁, R₂ and R₃ 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 alkylthio, a hydroxy, a hydroxyalkyl and an alkenyl, or R₁ and R₂ taken together form a substituted or unsubstituted aryl; and salts corresponding thereto.

The purine compounds have a formula:



wherein X is nitrogen or C-R₃ and Y is nitrogen or C-R₄ and R₁, R₂, R₃ and R₄ 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 amidoalkyl, an alkylthio, an alkenyl or a hydroxalkyl.

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

The oxygen bleaching agents of the compositions include organic peroxy acids diacylperoxides, inorganic peroxygen compounds and peracid precursors.

Peracids

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- α -naphthoic acid, and magnesium monoperoxyphthalate,

ii) aliphatic and substituted aliphatic monoperoxy acids, e.g., peroxy lauric acid, peroxy stearic acid, epsilon-phthalimido-peroxyhexanoic acid and o-carboxybenzamide peroxyhexanoic acid, N-nonylamidoperadipic acid and N-nonylamidopersuccinic acid,

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.

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; diperoxysebacic acid and diperoxy-isophthalic acid

viii) 2-decyldiperoxybutan-1,4-dioic acid

ix) N,N¹-terephthaloyl-di(6-aminopercaproic acid).

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,N¹-terephthaloyl-di(6-aminopercaproic acid).

A typical diacylperoxide useful herein includes dibenzoylperoxide.

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

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.

Typical examples of precursors are polyacylated alkylene diamines, such as N,N,N¹,N¹-tetraacetyl ethylene

diamine (TAED) and N,N,N',N'-tetraacetylmethylene diamine (TAMD); acylated glycolurils, such as tetraacetyl glycoluril (TAGU); triacetylcyanurate, sodium sulfophenyl ethyl carbonic acid ester, sodium acetyloxybenzene 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.

Preferred peroxygen bleach precursors are sodium p-benzoyloxybenzene sulfonate, N,N,N',N'-tetraacetylmethylene diamine, sodium nonanoyloxybenzene sulfonate and choline sulfophenyl carbonate.

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 composition 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.

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.

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

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

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.

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.

Suitable examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, including layered silicates such 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.

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, alkanedihydroxyphosphonates, 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.

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

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.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetetraacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexaacetates, diethylenetriaminepentaacetates, ethylenediamine disuccinate, and ethanol diglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

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.

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.

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

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.

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

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.

Preferred surfactants are one or a mixture of:

Anionic surfactants

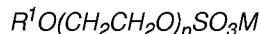
Anionic synthetic detergents can be broadly described as surface active compounds with one or more negatively charged functional groups. An important class of anionic compounds are the water-soluble salts, particularly the alkali metal salts, of organic sulfur reaction products having in their molecular 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



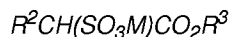
where R^1 is a primary alkyl group of 8 to 18 carbon atoms and M is a solubilizing cation. The alkyl group R^1 may have a mixture of chain lengths. It is preferred that at least two thirds of the R^1 alkyl groups have a chain length of 8 to 14 carbon atoms. This will be the case if R^1 is coconut alkyl, 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



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



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



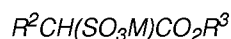
where R^4 is an alkyl group of 8 to 18 carbon atoms, Ar is a benzene ring (C_6H_4) and M is a solubilizing cation. The group R^4 may be a mixture of chain lengths. Straight chains of 11 to 14 carbon atoms are preferred.

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 alkylencarboxylate 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.

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.

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.

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



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:



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.

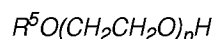
Nonionic surfactants

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.

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:



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.

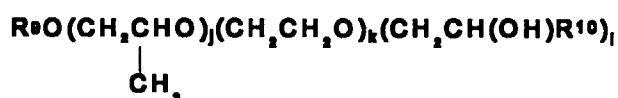
The average value of n should be at least 2. The numbers of ethylene oxide residues may be a statistical distribution around the average value. However, as is known, the distribution can be affected by the manufacturing process or altered by fractionation after ethoxylation. Particularly preferred ethoxylated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

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



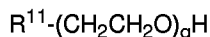
wherein R^6 is a linear alkyl hydrocarbon radical having an average of 6 to 18 carbon atoms, R^7 and R^8 are each linear alkyl hydrocarbons of about 1 to about 4 carbon atoms, x is an integer of from 1 to 6, y is an integer of from 4 to 20 and z is an integer from 4 to 25.

One preferred nonionic surfactant of the above formula is Poly-Tergent SLF-18⁷ 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 l is an integer having a value of from 1 to about 3. Most preferred are compositions 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.

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

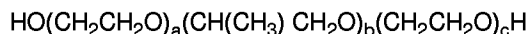


wherein R^{11} is a C_6 - C_{24} linear or branched alkyl hydrocarbon radical and q is a number from 2 to 50; more preferably R^{11} is a C_8 - C_{18} linear alkyl mixture and q is a number from 2 to 15.

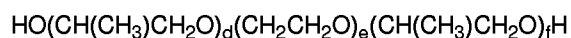
polyoxyethylene or polyoxypropylene condensates of alkyl phenols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to 12 carbon atoms and incorporating from about 2 to about 25 moles of ethylene oxide and/or propylene oxide.

polyoxyethylene derivatives of sorbitan 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, sorbitol 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.

polyoxyethylene-polyoxypropylene block copolymers having formula:



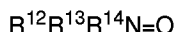
or



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.

Amine oxides having formula:

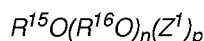


wherein R^{12} , R^{13} and R^{14} are saturated aliphatic radicals or substituted saturated aliphatic radicals. Preferable amine oxides are those wherein R^{12} is an alkyl chain of about 10 to about 20 carbon atoms and R^{13} and R^{14} are methyl or ethyl groups or both R^{12} and R^{13} are alkyl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

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, sulphy, sulphato, phosphato or phosphono. Examples of compounds falling within this definition are sodium 3-dodecylamino propionate and sodium 2-dodecylamino propane sulfonate.

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, sulphy, 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



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.

Examples of commercially available materials from Henkel Kommanditgesellschaft Aktien of Dusseldorf, Germany include APG⁷ 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; APG⁷ 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 APG⁷ 600 with R^{15} being C_{12} - C_{14} , n is 0 and p is 1.3.

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.

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

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

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%.

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

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.

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.

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.

Conventional stabilizers such as long-chain calcium and sodium soaps and C₁₂ to C₁₈ 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

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

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., Alcalase[®], Savinase[®] and Esperase[®] from Novo Industries A/S and Purafect OxP, ex. Genencor), amylases (e.g., Termamyl[®] and Duramyl[®] from Novo Industries and Purafect OxAm, ex. Genencor) and lipases (e.g. Lipolase[®] from Novo Industries).

Optional Ingredients

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.

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

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%

¹an acrylate/maleate copolymer from BASF

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

³nonionic surfactant supplied by BASF.

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

⁵incorporated via dissolution in the surfactant.

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 TiO₂ (0.1%) was incorporated into the base liquid.

A second composition (B) was also prepared except the TiO₂ was not incorporated. These two formulations were stored at ambient temperature and at 45°C for at least 14 weeks.

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.

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 TiO₂.

Example 2

The following inventive Sample (C) was prepared.

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

(continued)

Ingredient	% by Weight-Sample C
Sorbitol	6.0
Borax	3.0
Sokalan CP-7	5.0
Plurafac LF 403	2.0
Suspended TPCAP	1.7
BTA	0.05
TiO ₂	0.1

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

A second Sample D was prepared, which was identical to Sample C except for the fact that TiO₂ was not incorporated into the base liquid. These two formulations were stored at 40°C as described in Example 1.

After one week at 40°C there was no visible discoloration of Sample C containing TiO₂. 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) 0.001 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 triazole 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-nonylamidoperoxyadipic 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.

5 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.

10

15. A detergent composition 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.

15 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:

20

(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

25

2. substantially cleaning the dishware in the dishwasher.

30

35

40

45

50

55