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(54) MACHINE DISHWASHING GEL COMPOSITIONS

GELFÖRMIGE MASCHINENGESCHIRRSPÜLMITTEL

COMPOSITION DE GEL DETERGENT POUR MACHINE A LAVER LA VAISSELLE

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(73) Proprietors:
- **UNILEVER N.V.**
3013 AL Rotterdam (NL)
Designated Contracting States:
DE ES FR IT
- **UNILEVER PLC**
London EC4P 4BQ (GB)
Designated Contracting States:
GB

(72) Inventors:
- **SECEMSKI, Isaac, Israel**
Edgewater, NJ 07020 (US)
- **NICHOLSON, John, Richard**
45 River Road Edgewater, NJ 07020 (US)
- **PIATEK, Bozena, Marianna**
45 River Road Edgewater, NJ 07020 (US)
- **TOMLINSON, Alan, Digby Unilever Research**
NL-3133 AT Vlaardingen (NL)

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

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Description

Field of the Invention

[0001] The present invention relates to machine dishwashing gel compositions that have good viscosity and thixotropic profiles and deliver high performance cleaning.

Background of the Invention

[0002] Automatic dishwashing detergents for home use have traditionally been in powder or granulate form. More recently, the market-place 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.

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

[0003] 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.

[0004] 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.

[0005] Conversely, there are situations where the product should have low viscosity. A low viscosity is desirable for easy dispensing of product from its bottle.

[0006] Thixotropic liquids generally maintain high viscosity for storage but revert to lower viscosity under influence of applied shear. Thixotropy is shear thinning behavior that is time dependent in both its decrease in viscosity under applied shear and its regain of viscosity after cessation of shearing. Thus, appropriate thixotropic properties ensure that a machine dishwashing composition will be retained in a dispenser cup without leakage yet will be pourable from its bottle.

[0007] The earliest approaches to problems involving formulating thixotropic liquids in an optimum viscosity range involved the use of clays. Typical of this technology are the compositions disclosed in US-A-4,116,849. Although generally acceptable, clay structured liquids have a number of disadvantages. Montmorillonite clays, even in the presence of stabilizing agents, are sensitive to ionic strength. They lose their liquid structuring efficiency at the high electrolyte levels normally present in autodish liquid detergents. Clays tend to collapse onto themselves, or flocculate under these conditions. If this collapse occurs to any large extent during prolonged storage, the liquid will lose its physical stability, suffer syneresis and/or settling of solids. Collection of solids at the bottom of the container can lead to the formation of paste-like plugs which are difficult to dispense.

[0008] Attapulgite clay particles suspended in liquids tend to scatter light. Any large amount of these clay particles will thus impart a muddy dull color to the liquid. Furthermore, clays, being insoluble minerals, can adversely affect glass appearance. Deposition of clay onto the surface of glassware has been known to lead to spotting and filming.

[0009] Another problem of suspended solids in prior art liquids is that they are subject to recrystallization during storage periods. Through a process of Ostwald ripening, the solids can redistribute themselves in terms of number and size of crystals. These changes can cause a drastic change in rheology of the liquid over time. Poor stability and/or cup retention result.

[0010] Many polymers are known for their thickening properties. Within the machine dishwashing art, polyacrylic acid type polymers have been included as an important component but not necessarily to function as a thickener.

[0011] Use of polymers for gel-formation in liquid detergent compositions was suggested in US-A-3,060,124. Apparently, cross-linked vinyl polymers are primarily suitable. Hydrolyzed polyacrylonitrile cross-linked with formaldehyde was found particularly effective at stabilizing the gels against separation. US-A-4,228,048 illustrates the use of polyallyl sucrose cross-linked polyacrylates, commercially available under the trademark Carbopol®, as a thickener for liquid cleaning and bleaching concentrates. Japanese Laid Open Patents 59-36198 and 59-36200 further illustrate the use of polyacrylate cross-linked with compounds such as allylated pentaerythritol. These thickened formulas are used to suspend water-insoluble abrasives such as silicone dioxide and aluminum oxide.

[0012] 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.

[0013] 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).

[0014] It has now been found that effective machine dishwashing gels with acceptable viscosity profiles and that deliver high cleaning performance can be prepared containing oxygen bleach systems and a dual component structuring system including a carboxylate and an azole compound, especially an aromatic triazole.

[0015] It has unexpectedly been discovered that the azoles act as a co-structurant, increasing the viscosity of gels structured with cross-linked polycarboxylate structurants. Thus, gels with acceptable viscosity profiles can be formulated with azoles that contain lower levels of salt and structurant than would be possible without this molecule. However, formulating gels with these azole compounds can be complicated since the addition of a triazole molecule like benzotriazole to a gel with acceptable viscosity characteristics can result in an unacceptably thick product, often with a high level of crystal formation, not seen in the absence of the azole compound. Formulation rules leading to acceptable gel properties are defined. In addition, these gels exhibit a secondary benefit in delivering acceptable anti-silver tarnishing properties.

[0016] Azoles have traditionally been used as anticorrosion agents, such as for metal parts such as engine jackets and the like is described in US-A-4,649,025. Aromatic triazoles, such as benzotriazole, are particularly known to be effective in preventing silver tarnishing in general. Thus, GB-A-1180437 teaches high phosphate systems with surfactant to clean non-ferrous metals; US-A-5,110,494 deals with systems for industrial cleaning of aluminum; US-A-4,518,585 for a sterilizing system for dental and medical equipment;

US-A-4,199,483 and US-A-4,321,166 for high surfactant systems for fabrics washing; JO-4359097 and JO-5279700 for a high surfactant system for washing surgical appliances. None of this art is relevant to machine dishwashing.

[0017] Regarding the use of triazoles in machine dishwashing, WO-95/01416 describes a combination of a branched paraffin oil and a benzotriazole molecule, along with delaying the release of the oxygen bleach, to reduce silver tarnishing during machine dishwashing, and EP-A-124,815 describes the value of benzotriazole as a silver protection agent in machine dishwashing. However, inclusion of aromatic triazoles into machine dishwashing gels is not described in the prior art, especially relating to maintaining good physical stability and viscosity characteristics. In addition, there is no prior art teaching use of azoles as structuring agents, particularly in machine dishwashing.

Summary of the Invention

[0018] The present invention relates to a machine dishwashing gel composition which contains an effective amount of an oxygen bleaching agent, from 10 to 50% by weight of a builder material and from 0.2 to 2.0% by weight of a dual component structuring system consisting of a cross-linked polyacrylate structurant and an azole co-structurant. The components of the dual component structuring system are present in the compositions in an amount calculated on the type and level of the builder material also incorporated in the formulas. Thus, the invention relates to the ability of azoles, particularly aromatic triazoles, to act as co-structurants in combination with a cross-linked polycarboxylate structurant, enhancing the viscosity of gels structured with this polymer. The composition has a viscosity and shear-thinning profile consistent with good dispensing via squeezing through an orifice or pouring from a spout as well as retention in the dispensing cup of the dishwashing machine prior to cup opening. A method of processing such a gel formulation is also described.

[0019] 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 dual component structuring system is preferably composed of a high molecular weight cross-linked polycarboxylate, most preferably a cross-linked polyacrylate, and an aromatic azole, preferably a triazole.

Brief Description of the Drawings

[0020]

Fig. 1 is a graph of the viscosity profile of a machine dishwashing gel having a mixture of carboxylate builders without the azole compound of the dual component structuring system of the invention.
Fig. 2 is a graph of the viscosity profile of a machine dishwashing gel having a mixture of carboxylate builders with the inventive dual component structuring system.
Fig. 3 is a graph of the viscosity profile of a machine dishwashing gel having a phosphate builder, but without the azole compound of the dual component structuring system of the invention.
Fig. 4 is a graph of the viscosity profile of a machine dishwashing gel having a phosphate builder, but with the inventive dual component structuring system.

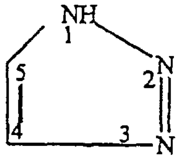
Detailed Description of the Preferred Embodiments

[0021] The detergent gel compositions of the invention comprise from 10 to 50% by weight of a builder, an effective amount of an oxygen bleaching agent and from 0.2 to 2.0% by weight of a dual component structuring system consisting of a cross-linked polycarboxylate structurant and an azole as described below.

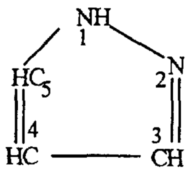
Dual Component Structuring System

A. Azoles

[0022] Azoles useful as co-structurants in the invention are nitrogen containing heterocylic 5-membered ring compounds which are present in a level of from 0.01% to 0.5% by weight, preferably from 0.01% to 0.2% 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, herein incorporated by reference.
[0023] 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:

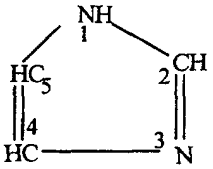


[0024] Suitable triazoles include benzotriazole; tolyltriazole; 4-phenyl-1,2,3-triazole; 1,2-naphthotriazole and 4-nitrobenzotriazole; and the like, especially preferred is benzotriazole.
[0025] The pyrazoles which can be used in the composition of this invention include water-soluble pyrazoles such 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:



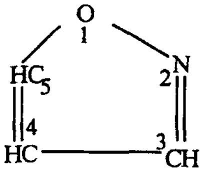
[0026] Suitable pyrazoles include pyrazole; 3,5-dimethyl pyrazole; 6-nitroindazole, 4-benzyl pyrazole; 4,5-dimethyl pyrazole; and 3-allyl pyrazole; and the like.
[0027] Imidazoles which can be used in the composition of this invention include water-soluble imidazoles such as imidazole itself or a substituted 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:



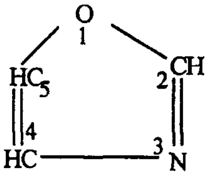
[0028] Suitable imidazoles which can be employed in the composition of this invention include imidazole; adenine; guanine; benzimidazole; 5-methyl benzimidazole; 2-phenyl imidazole; 2-benzyl imidazole; 4-allyl imidazole; 4-(betahydroxy ethyl)-imidazole; purine; 4-methyl imidazole; xanthine; hypoxanthine; 2-methyl imidazole; and the like.

[0029] 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:



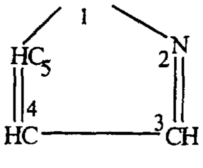
[0030] Suitable isoxazoles include isoxazole; 3-mercaptoisoxazole; 3-mercaptobenzisoxazole; benzisoxazole; and the like.

[0031] 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:



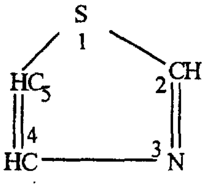
[0032] Suitable oxazoles include oxazole; 2-mercaptaxazole; 2-mercaptobenzoxazole; and the like.

[0033] 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:



[0034] Suitable isothiazoles include isothiazole; 3-mercaptoisothiazole; benzoisothiazole and the like.

[0035] 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:

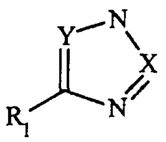


[0036] Suitable thiazoles include thiazole; 2-mercaptothiazole; 2-mercaptobenzothiazole; benzothiazole and the like.

[0037] 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.

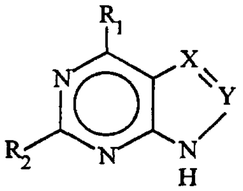
[0038] Specific 1,3 N-azoles which are useful include those azoles described in US-A-5,480,576 and US-A-5,468,410, herein incorporated by reference.

[0039] 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.

[0040] 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.

[0041] 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.

B. Cross-linked Polyacrylate Structurant

[0042] The structurant of the dual component structuring system 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.

[0043] 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 about 4,000,000, are particularly preferred.

[0044] Polymeric carboxylic acids described in GB-A-2,164,350; US-A- 4,859,358 and US-A-4,836,948 are also useful in the invention and are incorporated by reference.

[0045] The amount of cross-linked polyacrylate present as the structurant is dependent on the type and amount of builder material incorporated in the compositions.

[0046] For example if the builder material is primarily a monomeric carboxylate, polymeric carboxylate or mixtures thereof, the polyacrylate structurant should be present in the amount of 0.5% to 2.0% wt, preferably 0.8% to 1.7% wt.

[0047] If the builder material is primarily a mixture of phosphate salts, the polyacrylate structurant should be present in an amount of 0.2% to 1.7% wt, preferably 0.5% to 1.5% wt.

[0048] Additionally, the total amount of builder material and cross-linked polycarboxylate structurant should fall within a prescribed range which is dependent on the type of builder used and is calculated by the following formula:

$$\text{wt. \% of builder x wt. \% of structurant}$$

[0049] If the builder is a monomeric carboxylate, polymeric carboxylate or mixtures thereof the product of the weight percent builder and weight percent structurant, as indicated in the above formula, should not exceed 60, preferably is 20 to 50, most preferably is 25 to 45.

[0050] If the builder is one or a mixture of phosphate salts, the product of the weight percent builder and weight percent structurant, as indicated in the above formula, should be less than 40, preferably between 5 and 40, most preferably between 10 and 30.

Peroxy Bleaching Agents

[0051] The oxygen bleaching agents of the compositions include organic peroxy acids and diacylperoxides. 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, epsilon-phthalimido peroxyhexanoic acid and o-carboxybenzamido 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; and US S/N 08/210,973, herein incorporated by reference.
iv) Sulfonyl peroxyacids such as compounds described in US-A-5,039,447, herein incorporated by reference.

[0052] 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; diperoxyse bacic acid and diperoxy-isophthalic acid
viii)2-decyldiperoxybutan-1,4-dioic acid
ix) N,N^1-terephthaloyl-di(6-aminopercaproic acid).

[0053] A typical diacylperoxide useful herein includes dibenzoylperoxide.

[0054] 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.

[0055] Preferred oxygen bleaching agents include epsilon-phthalimido-peroxyhexanoic acid, o-carboxybenzaminoperoxyhexanoic acid, and mixtures thereof.

[0056] The oxygen bleaching agent is present in the composition in an amount from 1 to 20% by weight, preferably 1 to 15% by weight percent, most preferably 2 to 10% by weight.

[0057] 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 to produce stable capsules in alkaline liquid formulations.

[0058] A preferred encapsulation method is described in US-A-5,200,236, herein incorporated by reference. In the patented method, the bleaching agent is encapsulated as a core in a paraffin wax material having a melting point from about 40°C to 50°C. The wax coating has a thickness of from 100 to 1500 microns.

Bleach Precursors

[0059] 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.

[0060] 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.

[0061] Preferred peroxygen bleach precursors are sodium p-benzoyloxybenzene sulfonate, N,N,N^1,N^1-tetraacetylethylene diamine, sodium nonanoyloxybenzene sulfonate and choline sulfophenyl carbonate.

Deterrent Builder Materials

[0062] The compositions of this invention contains either organic builders, particularly carboxylates, or inorganic builders, particularly phosphorous containing compounds.

Phosphorus Containing Builders

[0063] Examples of phosphorus-containing inorganic builders include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates and polyphosphates, particularly ammonium and alkanol ammonium salts, and phosphonates. Particularly preferred phosphate builders include sodium and potassium tripolyphosphates, pyrophosphates, hexametaphosphates and trimetaphosphates.

[0064] When a phosphate builder is incorporated into the formula it is present in an amount of 10% to 50% by wt, most preferably 15 to 35% wt and the product of the weight percent builder and weight percent of cross-linked polycarboxylate structurant should not exceed 40, preferably between 5 and 40, most preferably between about 10 and about 30 as discussed above.

Non-phosphorus Inorganic Builders

[0065] Non-phosphorus-containing inorganic builders may be additionally used such as water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, layered silicates such as SKS-6 ex Hoechst, metasilicates, phytic acid, borate and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates, including layered silicates and zeolites.

Organic Builders

[0066] Organic detergent builders useful in the present invention including a variety of polycarboxylate compounds. As used herein "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least three (3) carboxylates. Monomeric or polymeric carboxylates are preferred. Such polycarboxylates include 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, herein incorporated by reference.

[0067] Alkali metal citrates, nitrilotriacetates, oxydisuccinates, polyphosphonates and acrylate/maleate copolymers and acrylate/maleate/vinyl alcohol terpolymers are especially preferred organic builders.

[0068] The foregoing detergent builders are meant to illustrate but not limit the types of builders that can be employed in the present invention.

[0069] 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, and polyhydroxysulfonates.

[0070] When the builder is comprised primarily of either monomeric or polymeric carboxylates or mixtures thereof the builder should be present in an amount of 10 to 45% wt, most preferably 15 to 40% wt. The product of the weight percent of carboxylate builder and the weight percent of polycarboxylate structurant should be less than 60, preferably 20 to 50, most preferably 25 to 45 as described above.

Sequestrants

[0071] 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.

[0072] Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraaminehexaacetates, diethylenetriaminepentaacetates, ethylenediamine disuccinate, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

[0073] 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.

[0074] 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.

[0075] If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such composition.

Anti-Sealants

[0076] 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.

[0077] 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 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

[0078] Useful surfactants include anionic, nonionic, cationic, amphoteric, zwitterionic types and mixtures of these surface active agents. Such surfactants are well known in the detergent art and are described at length in "Surface Active Agents and Detergents", Vol. II, by Schwartz, Perry & Berch, Interscience Publishers, Inc. 1959, herein incorporated by reference.

[0079] Preferred surfactants are one or a mixture of:

Anionic surfactants

[0080] 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

[0081]

$$R^1OSO_3M$$

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

[0082]

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

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

[0083]

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

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.

[0084] 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

[0085]

$$R^4ArSO_3M$$

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.

[0086] *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.

[0087] 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.

Nonionic surfactants

[0088] 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:

> *polyoxyethylene or polyoxypropylene condensates of aliphatic carboxylic acids,* whether linear- or branched-chain and unsaturated or saturated, 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.

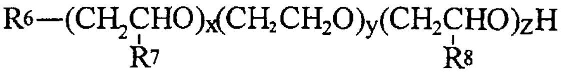
[0089] Ethoxylated fatty alcohols may be used alone or in admixture with anionic surfactants, especially the preferred surfactants above. The average chain lengths of the alkyl group R^5 in the general formula:

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

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.

[0090] 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.

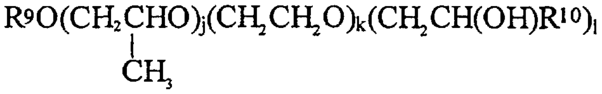
[0091] Also included within this category are nonionic surfactants having a formula:



$$R^6-(CH_2\underset{R^7}{\underset{|}{C}}HO)_x(CH_2CH_2O)_y(CH_2\underset{R^8}{\underset{|}{C}}HO)_zH$$

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.

[0092] One preferred nonionic surfactant of the above formula is Poly-Tergent SLF-18® 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



$$R^9O(CH_2\underset{CH_3}{\underset{|}{C}}HO)_j(CH_2CH_2O)_k(CH_2CH(OH)R^{10})_l$$

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 compositions in which j is 1, k is from about 10 to about 20 and 1 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 U.S. 4,340,766 to BASF.

[0093] 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.

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 or 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, sorbitan 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:

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

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.

[0094] *Amine oxides* having formula:

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

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.

[0095] *Amphoteric* synthetic detergents can be broadly described as derivatives of aliphatic and 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.

[0096] *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

[0097]

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

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 .

[0098] Examples of commercially available materials from Henkel Kommanditgesellschaft Aktien of Dusseldorf, Germany include APG® 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® 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® 600 with R^{15} being C_{12}-C_{14}, n is 0 and p is 1.3.

[0099] 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.

[0100] The amount of glycoside surfactant, anionic surfactant and/or ethoxylated fatty alcohol surfactant will be from 0.5 to 30% by weight of the composition. Desirably the total amount of surfactant lies in the same range. The preferred range of surfactant is from 0.5 to 20% by weight, more preferably from 0.5 to 10% by weight.

Filler

[0101] An inert filler material which is water-soluble may also be present in cleaning 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 about 2% to about 10% by weight of the cleaning composition.

Non-Carboxylic Thickening Agents

[0102] 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 about 10%, preferably 0.5 to 5%.

[0103] The amount of thickener employed in the compositions is from 0 to 5%, preferably 0.5-3%.

[0104] 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 about 0.01 to about 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

[0105] 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%. Preferred antifoam systems are described in Angevaare et al. 95-158-EDG, herein incorporated by reference.

Enzymes

[0106] 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).

Optional Ingredients

[0107] 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, herein incorporated by reference; colorants; perfumes; and other functional additives.

[0108] The following examples 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

[0109] A number of gel compositions having various levels of builder, polyacrylate and oxygen bleach were prepared as described in Table 1. Half of the samples were prepared with benzotriazole and half were prepared without it.

Table 1

Ingredient	% by Weight
Sodium citrate/Sokalan CP7[1]	25-35
Carbopol 627[2]	1.0-1.5
Glycerol/borax stabilizer	9.0
Enzymes	1.2
Plurafac LF 403[3]	2.0
Oxygen bleach encapsulates[4]	1.0-2.0
Benzotriazole[5]	0 or 0.05
deionized 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 Lang, U.S. Patent No. 5,200,236.

[5] incorporated via dissolution in the surfactant.

[0110] The viscosities (in mPas) of the gels were measured at 1 sec-1 and 20 sec -1 and any negatives regarding physical appearance (presence of crystals, lumpiness) were noted. An acceptable viscosity range for a machine dishwashing gel of this sort is 8,000-18,000 mPas at 1 sec-1 and 1,300-2,000 mPas at 20 sec-1.

[0111] The viscosity results are shown in Figures 1 (without benzotriazole) and 2 (with benzotriazole). Gels lying within the acceptable viscosity range are designated by open circles and those lying outside the range designated by closed circles. Those unacceptable gels at high builder and/or structurant level have a viscosity above the acceptable range at either 1 sec-1 or 20 sec-1 (or at both) and those unacceptable gels at low builder and/or structurant level have a viscosity below the acceptable range at either 1 sec-1 or 20 sec-1 (or at both).

[0112] A formulation region can be defined in which stable gels can be formulated with the correct viscosity profile. The addition of benzotriazole at a level as low as 0.05% dramatically shifts the acceptable formulation region to the area of lower builder and cross-linked polycarboxylate. This is a clear result of the ability of benzotriazole to act as a co-structurant and enhance the viscosity of the gel.

Example 2

[0113] The gel formulation in Example 1 was modified by replacing the citrate/polycarboxylate builder with potassium tripolyphosphate. Bases, with and without 0.05% BTA, were prepared and the viscosity results are shown in Figure 3 (without benzotriazole) and Figure 4 (with benzotriazole). As with the zero-P systems, benzotriazole acts as a co-structurant in phosphate systems.

Example 3

[0114] The pH of gels according to Example 1 with 35% builder and 1.5% cross-linked polycarboxylate, with and without benzotriazole, were reduced to pH 6.5. The viscosities of the gels with and without benzotriazole were the same (7,000 mPas at 1 sec-1 and 1,300 mPas at 20 sec-1) indicating that benzotriazole is preferably used as a co-structurant in systems above pH 6.5.

Example 4

[0115] In a different system based on Example 1 with 35% builder and 1.5% Carbopol, glycerol is replaced by sorbitol, the pH is reduced to 6.5 and the encapsulated oxygen bleach system is replaced by unencapsulated N,N'-terephthaloyl-di-6-amino percaproic acid (TPCAP). These gels, both with and without benzotriazole, had similar viscosities, again indicating that benzotriazole is preferably used as a co-structurant in formulations having a pH above 6.5.

Example 5

[0116] Gel formulations according to Example 1 containing 35% builder with and without 0.05% BTA, were tested for silver tarnishing. Silver forks, knives and spoons were evaluated in a standard European washing machine, using a normal 65°C cycle. Tarnishing was judged on a six-point scale; 0 for no tarnishing, 6 for heavy tarnishing. The results are given in Table 2.

Table 2

	Score		
	Fork	Knife	Spoon
Gel with BTA	1.0	1.0	1.0
Gel without BTA	5.0	6.0	4.0

[0117] Thus, BTA can deliver anti-tarnish benefits even after solubilization in a gel composition.

Example 6

[0118] The stability of amylase and protease in the Gels from Example 5 were evaluated at both room temperature and 40°C. The percent enzyme remaining after storage for 25 days is given in Table 3.

Table 3

	% Enzyme Remaining			
	Protease		Amylase	
	R.T.	40°C	R.T.	40°C
Gel with BTA	100	85	100	70
Gel without BTA	100	80	100	70

[0119] Thus, addition of BTA has no significant effect on enzyme stability in the gel.

Example 7

[0120] The effect of dissolved BTA on de-staining efficacy of gels was evaluated. The Gels in Example 5 were evaluated for tannin removal on stained tea cups in a standard European machine. BTA had no effect on the tea stain removal.

Example 8

[0121] Formulations were prepared according to Example 1 in which BTA was added either separately at the beginning of the processing; separately towards the end of the processing at the point when the surfactant is added just prior to the minor ingredients; or added along with the surfactant after prior dissolution in the surfactant.

[0122] It was found that when the BTA is added via prior dissolution into the surfactant, the viscosity of the gel reached equilibrium more rapidly. This is the most desirable option since it expedites processing allowing a more rapid assessment of the final viscosity profile.

Claims

1. A detergent gel composition for a machine dishwashing comprising:

   (a) from 10 to 50% by wt. of a builder material;

   (b) an effective amount of an oxygen bleaching agent;

   (c) from 0.2 to 2,0% by weight of a dual component structuring system consisting of a cross-linked polyacrylate structurant and an azole co-structurant provided that the total level of the builder and the structurant does not exceed 60 as calculated by the formula:-

   $$\text{wt. \% of builder x wt. \% of polyacrylate structurant} \leq 60.$$

2. A detergent composition according to claim 1, wherein the builder material is 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 and the structurant is present in an amount of 0.5 to 2.0% and the product of the weight percent of the builder and the weight percent of structurant is in the range from 20 to 50.

4. A detergent composition according to claim 1, wherein the azole costructurant 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 cross-linked polyacrylate structurant is a salt of polyacrylic acid having a molecular weight of from 300,000 to 6 million.

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

8. 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.

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

10. A detergent composition according to claim 9, 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.

11. A detergent composition according to claim 8, wherein the oxygen bleaching agent is wax encapsulated.

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

an enzyme.

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

14. A detergent composition according to claim 1 wherein the builder material is a water soluble salt of an alkali metal pyrophosphate, an orthophosphate, a polyphosphate and mixtures thereof.

15. A detergent composition according to claim 14 wherein the builder is present in an amount of from about 10 to 40% wt, the poly-acrylate structurant is present in an amount of from 0.2% to 1.7% wt and the product of the weight percent builder and the weight percent of the structurant is in the range from about 5 to 40.

16. A detergent composition according to claim 14 wherein the phosphate salt is selected from the group consisting of sodium tripolyphosphate, potassium tripolyphosphate, pyrophosphate, hexametaphosphate, trimetaphosphates and mixtures thereof.

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

a) adding to a wash liquor an effective amount of a detergent composition comprising:

i) from 10 to 50% by wt. of a builder material;
ii) an effective amount of an oxygen bleaching agent;
iii) from 0.2 to 2.0% by weight of a dual component structuring system consisting of a cross-linked poly-acrylate structurant and an azole co-structurant provided that the total amount of the builder and the structurant does not exceed 60 as calculated by the formula:

$$\text{wt. \% of builder x wt. \% of structurant} \leq 60;$$

and

b) cleaning the dishware in a machine dishwasher.

Patentansprüche

1. Waschmittelgelzusammensetzung zum maschinellen Geschirrwaschen, umfassend:

(a) 10 bis 50 Gewichtsprozent eines Buildermaterials;
(b) eine wirksame Menge eines Sauerstoffbleichmittels;
(c) 0,2 bis 2,0 Gewichtsprozent eines strukturierenden Zweikomponenten-Systems, bestehend aus einem vernetzten Polyacrylat-Strukturierungsmittel und einem Azol-Costrukturierungsmittel, mit der Maßgabe, dass die Gesamtmenge von dem Builder und dem Strukturierungsmittel 60, wie berechnet durch die Formel:

$$\text{Gewichtsprozent Builder x Gewichtsprozent Polyacrylat-Strukturierungsmittel} < 60,$$

nicht übersteigt.

2. Waschmittelzusammensetzung nach Anspruch 1, wobei das Buildermaterial aus der Gruppe eines monomeren Carboxylats, polymeren Carboxylats und Gemischen davon ausgewählt ist.

3. Waschmittelzusammensetzung nach Anspruch 2, wobei der Builder in einer Menge von 10 bis 45 Gewichtsprozent vorliegt und das Strukturierungsmittel in einer Menge von 0,5 bis 2,0% vorliegt und das Produkt der Gewichtsprozent Builder und Gewichtsprozent Strukturierungsmittel im Bereich von 20 bis 50 liegt.

4. Waschmittelzusammensetzung nach Anspruch 1, wobei das AzolCostrukturierungsmittel ein Triazolazol ist.

5. Waschmittelzusammensetzung nach Anspruch 4, wobei das Triazol Benzotriazol ist.

6. Waschmittelzusammensetzung nach Anspruch 1, wobei das vernetzte Polyacrylat-Strukturierungsmittel ein Salz von Polyacrylsäure mit einem Molekulargewicht von 300000 bis 6 Millionen ist.

7. Waschmittelzusammensetzung nach Anspruch 1, wobei das Sauerstoffbleichmittel in einer Menge von 1 bis 20 Gewichtsprozent vorliegt.

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

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

10. Waschmittelzusammensetzung nach Anspruch 9, wobei die substituierten aliphatischen Monoperoxysäuren aus der Gruppe, bestehend aus ε-Phthalimido-peroxyhexansäure, o-Carboxybenzamidoperoxyhexansäure, N-Nonylamidoperadipinsäure, N-Nonylamidoperbernsteinsäure und Gemischen davon, ausgewählt sind.

11. Waschmittelzusammensetzung nach Anspruch 8, wobei das Sauerstoffbleichmittel in Wachs eingekapselt ist.

12. Waschmittelzusammensetzung nach Anspruch 1, wobei die Zusammensetzung weiterhin eine wirksame Menge eines Enzyms umfasst.

13. Waschmittelzusammensetzung nach Anspruch 1, die weiterhin 0,5 bis 30 Gewichtsprozent eines Tensids umfasst.

14. Waschmittelzusammensetzung nach Anspruch 1, wobei das Buildermaterial ein wasserlösliches Salz eines Alkalimetallpyrophosphats, eines -orthophosphats, eines -polyphosphats und Gemischen davon ist.

15. Waschmittelzusammensetzung nach Anspruch 14, wobei der Builder in einer Menge von etwa 10 bis 40 Gewichtsprozent vorliegt, das Polyacrylat-Strukturierungsmittel in einer Menge von 0,2% bis 1,7 Gewichtsprozent vorliegt und das Produkt der Gewichtsprozent Builder und der Gewichtsprozent Strukturierungsmittel im Bereich von etwa 5 bis 40 liegt.

16. Waschmittelzusammensetzung nach Anspruch 14, wobei das Phosphatsalz aus der Gruppe, bestehend aus Natriumtripolyphosphat, Kaliumtripolyphosphat, -pyrophosphat, -hexametaphosphat, -trimetaphosphaten und Gemischen davon, ausgewählt ist.

17. Verfahren zum Reinigen von Geschirr in einer Geschirrspülmaschine, umfassend die Schritte:

a) Zugeben zu einer Waschlauge einer wirksamen Menge einer Waschmittelzusammensetzung, umfassend:

(i) 10 bis 50 Gewichtsprozent eines Buildermaterials;
(ii) eine wirksame Menge eines Sauerstoffbleichmittels;
(iii) 0,2 bis 2,0 Gewichtsprozent eines strukturierenden Zweikomponenten-Systems, bestehend aus einem vernetzten Polyacrylat-Strukturierungsmittel und einem Azol-Costrukturierungsmittel, mit der Maßgabe, dass die Gesamtmenge von dem Builder und dem Strukturierungsmittel 60, wie berechnet durch die Formel:

$$\text{Gewichtsprozent Builder x Gewichtsprozent Strukturierungsmittel} \leq 60,$$

nicht übersteigt und
b) Reinigen des Geschirrs in einer Geschirrspülmaschine.

Revendications

1. Composition détergente gel destinée au lavage de la vaisselle en machine et comprenant :

(a) de 10 à 50 % en poids d'un matériau édificateur ;

(b) une quantité efficace d'un agent blanchissant oxygène ;

(c) de 0,2 à 2,0 % en poids d'un système structurant à deux composants composé d'un structurant polyacrylate réticulé et d'un co-structurant azole, à condition que le niveau total de l'édificateur et du structurant ne dépasse pas 60, comme calculé selon la formule suivante :

$$\text{\% en poids de l'édificateur x \% en poids de structurant polyacrylate} \leq 60$$

2. Composition détergente selon la revendication 1, dans laquelle le matériau édificateur est sélectionné à partir du groupe composé d'un carboxylate monomère, d'un carboxylate polymère et de mélanges de ceux-ci.

3. Composition détergente selon la revendication 2, dans laquelle l'édificateur est présent dans une quantité allant de 10 à 45 % en poids et dans laquelle le structurant est présent dans une quantité allant de 0,5 à 2,0 % en poids, et le produit du pourcentage en poids de l'édificateur et du pourcentage en poids du structurant est compris dans la gamme allant de 20 à 50.

4. Composition détergente selon la revendication 1, dans laquelle le co-structurant azole est un azole triazole.

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

6. Composition selon 1 a revendication 1, dans laquelle le structurant polyacrylate réticulé est un sel d'acide polyacrylique ayant une masse moléculaire moyenne allant de 300.000 à 6 millions.

7. Composition détergente selon la revendication 1, dans laquelle l'agent blanchissant oxygène est présent dans une quantité allant de 1 à 20 % en poids.

8. Composition détergente selon la revendication 1, dans laquelle l'agent blanchissant oxygène est sélectionné à partir du groupe composé des peroxy acides organiques, des peroxydes de diacyle et des mélanges de ceux-ci.

9. Composition détergente selon la revendication 8, dans laquelle les peroxy acides organiques sont sélectionnés à partir du groupe composé de l'acide peroxybenzoïque, des monoperoxy acides aliphatiques, des monoperoxy acides aliphatiques substitués et des mélanges de ceux-ci.

10. Composition détergente selon la revendication 9, dans laquelle les monoperoxy acides aliphatiques substitués sont sélectionnés à partir du groupe composé de l'acide epsilone-phthalimido-peroxyhexanoïque, l'acide o-carboxybenzamido peroxyhexanoïque, l'acide N-nonylamidopéradipique, l'acide N-nonylamidopersuccinique et des mélanges de ceux-ci.

11. Composition détergente selon la revendication 8, dans laquelle l'agent blanchissant oxygène est encapsulé dans de la cire.

12. Composition détergente selon la revendication 1, dans laquelle la composition comprend en outre une quantité efficace d'une enzyme.

13. Composition détergente selon la revendication 1, comprenant en outre de 0,5 à 30 % en poids d'un tensioactif.

14. Composition détergente selon la revendication 1, dans laquelle le matériau édificateur est un sel soluble dans l'eau d'un pyrophosphate, d'un orthophosphate, d'un polyphosphate de métal alcalin, et des mélanges de ceux-ci.

15. Composition détergente selon la revendication 14, dans laquelle l'édificateur est présent dans une quantité allant d'environ 10 à 40 % en poids, le structurant est présent dans une quantité allant de 0,2 à 1,7 % en poids et dans laquelle le produit du pourcentage d'édificateur par le pourcentage du structurant est compris dans la gamme allant d'environ 5 à 40.

16. Composition détergente selon la revendication 14, dans laquelle le sel de phosphate est sélectionné à partir du groupe composé du tripolyphosphate de sodium, du tripolyphosphate de potassium, du pyrophosphate, de l'hexamétaphosphate, des trimétaphosphates et des mélanges de ceux-ci.

17. Procédé de nettoyage de la vaisselle dans une machine à laver la vaisselle comprenant les étapes consistant à :

(a) ajouter à la liqueur de lavage une quantité efficace d'une composition détergente comprenant :

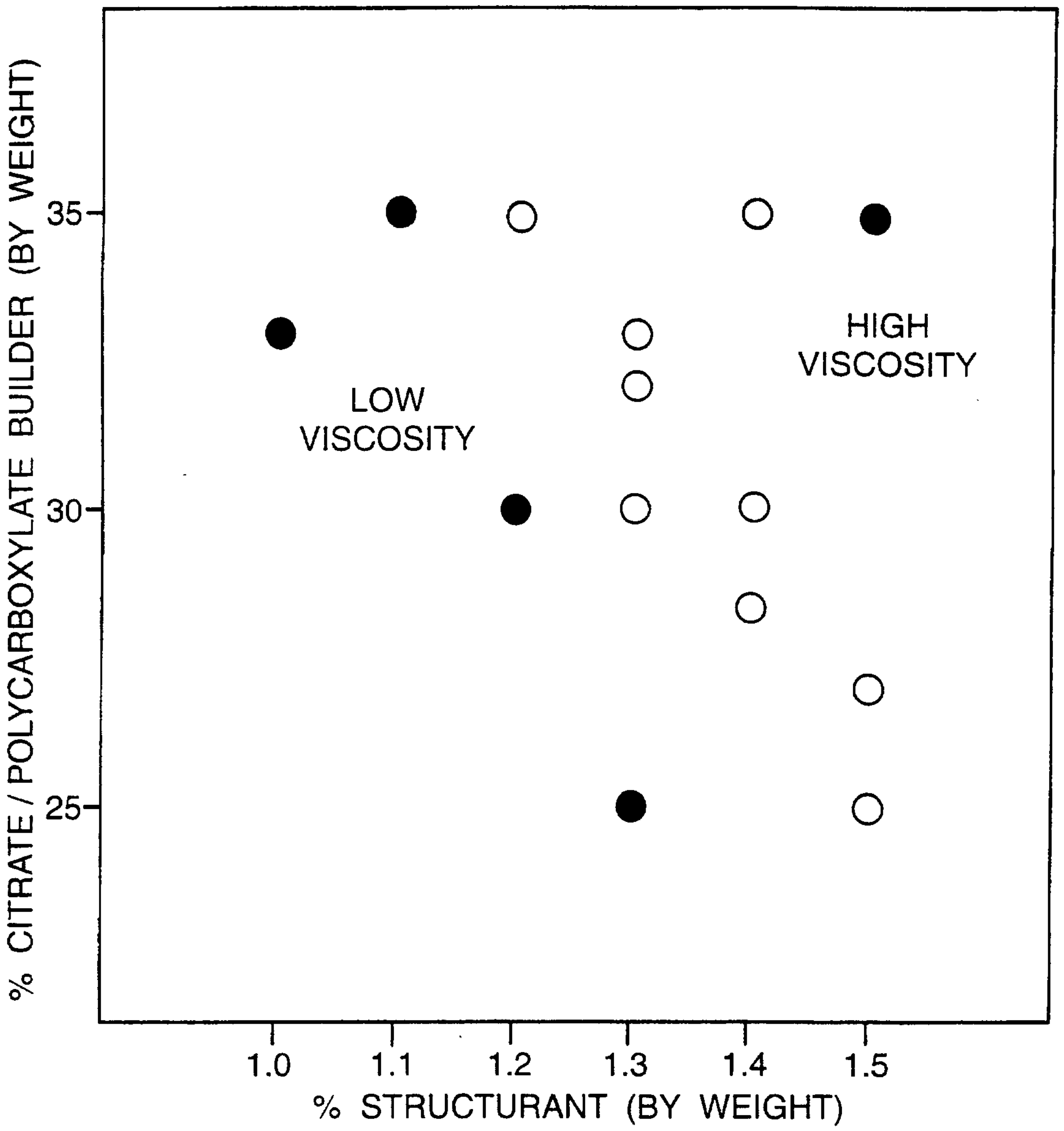
i) de 10 à 50 % en poids d'un matériau édificateur ;
ii) une quantité efficace d'un agent blanchissant oxygène ;
iii) de 0,2 à 2,0 % en poids d'un système structurant à deux composants composé d'un structurant polyacrylate réticulé et d'un structurant azole, à condition que la quantité totale de l'édificateur et du structurant ne dépasse pas 60, comme calculé selon la formule suivante:

$$\%\text{ en poids d'édificateur x }\%\text{ en poids de structurant} \leq 60$$

et

b) laver la vaisselle dans une machine à laver.

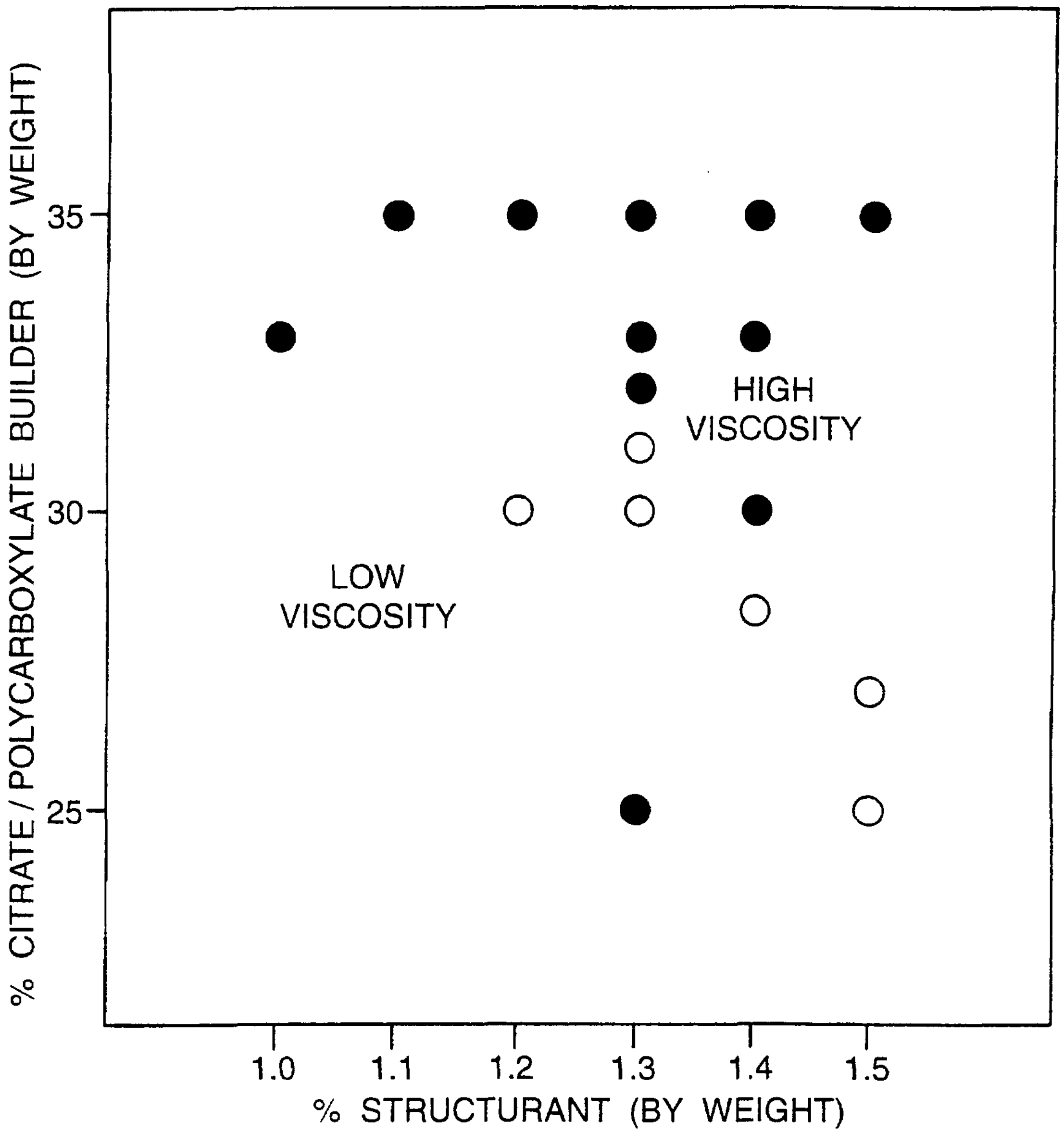
Fig.1.



○ GELS HAVE VISCOSITY OF 1,300-2,000 mPa*s AT 20 / SEC AND 8,000-17,000 mPa*s AT 1 / SEC

● GELS HAVE VISCOSITY OUTSIDE RANGE OF 1,300-2,000 mPa*s AT 20 / SEC AND / OR 8,000-17,000 mPa*s AT 1 / SEC

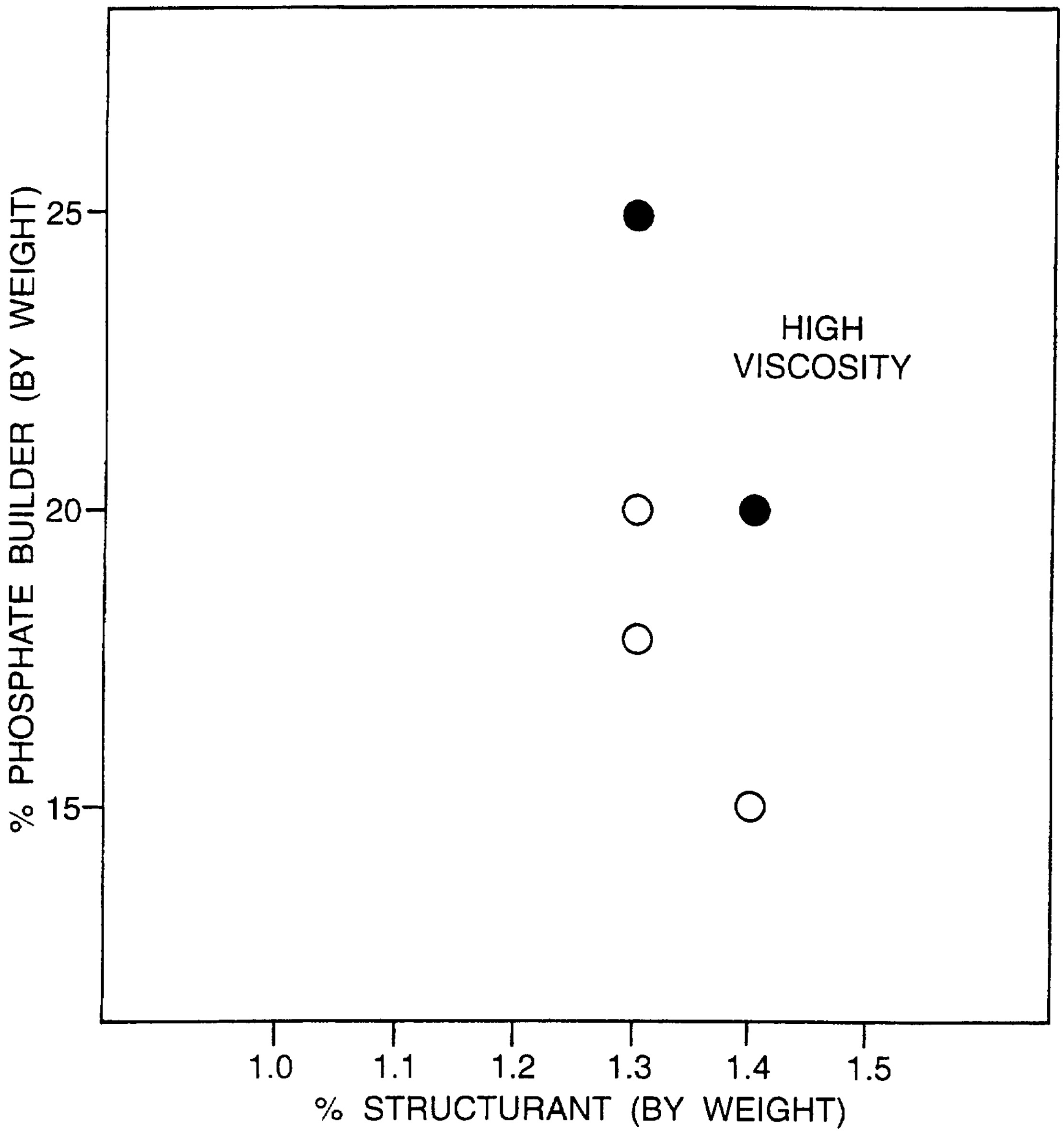
Fig.2.



○ GELS HAVE VISCOSITY OF 1,300-2,000 mPa*s AT 20 / SEC AND 8,000-17,000 mPa*s AT 1 / SEC

● GELS HAVE VISCOSITY OUTSIDE RANGE OF 1,300-2,000 mPa*s AT 20 / SEC AND / OR 8,000-17,000 mPa*s AT 1 / SEC

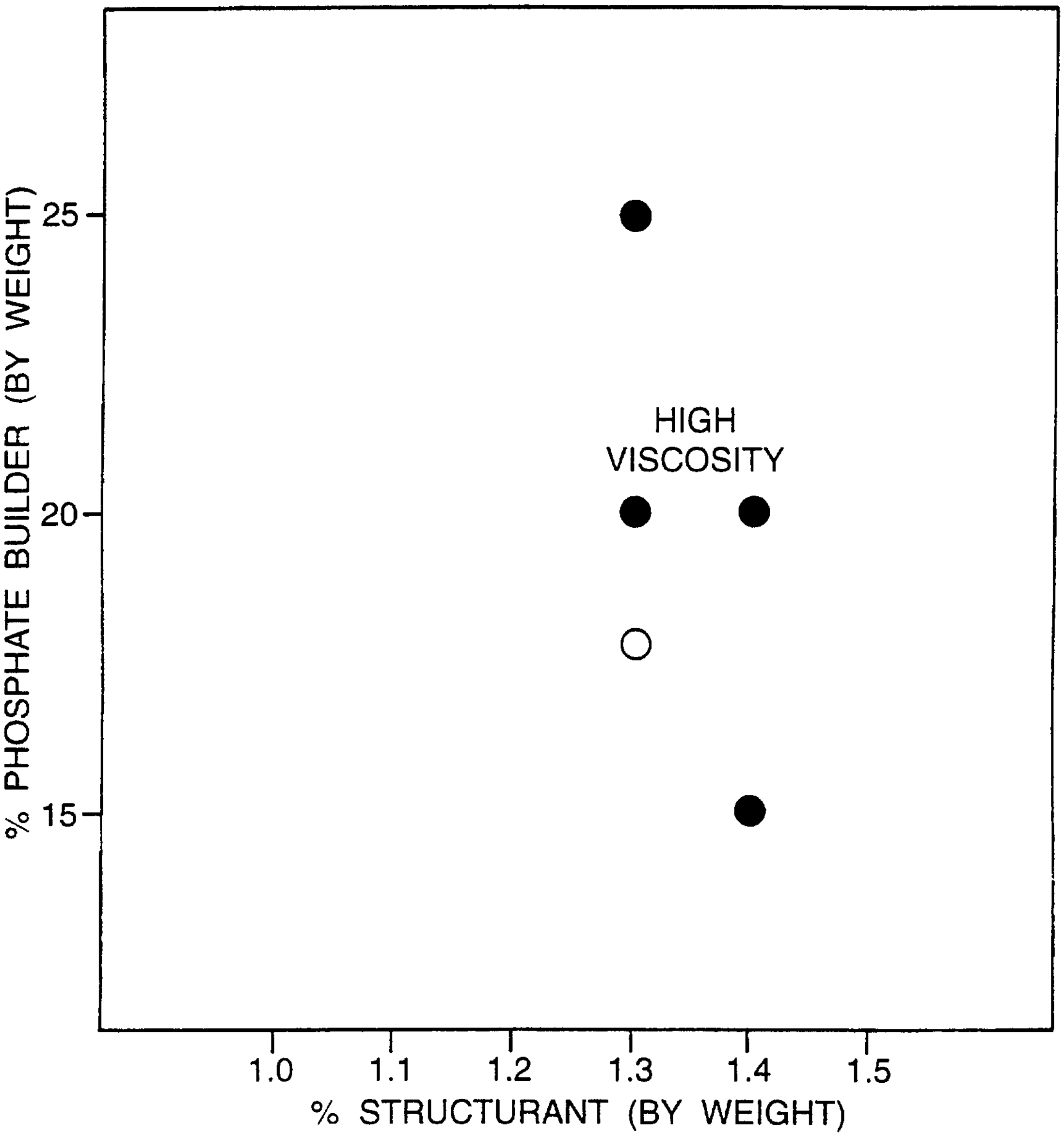
Fig.3.



○ GELS HAVE VISCOSITY OF 1,300-2,000 mPa*s AT 20 / SEC AND 8,000-17,000 mPa*s AT 1 / SEC

● GELS HAVE VISCOSITY OUTSIDE RANGE OF 1,300-2,000 mPa*s AT 20 / SEC AND / OR 8,000-17,000 mPa*s AT 1 / SEC

Fig.4.



○ GELS HAVE VISCOSITY OF 1,300-2,000 mPa*s AT 20 / SEC AND 8,000-17,000 mPa*s AT 1 / SEC

● GELS HAVE VISCOSITY OUTSIDE RANGE OF 1,300-2,000 mPa*s AT 20 / SEC AND / OR 8,000-17,000 mPa*s AT 1 / SEC