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(54) **CONCENTRATED NIL-PHOSPHATE LIQUID AUTOMATIC DISHWASHING DETERGENT
COMPOSITIONS CONTAINING ENZYME**

KONZENTRIERTES PHOSPHATFREIES FLÜSSIGES ENZYMHALTIGES
MASCHINENGESCHIRRSPÜLMITTEL

COMPOSITIONS DETERGENTES DE LAVAGE AUTOMATIQUE DE VAISSELLE LIQUIDES
CONCENTREES SANS PHOSPHATE CONTENANT UNE ENZYME

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EP-A- 0 234 867 **WO-A-93/21299**
DE-A- 2 038 103 **DE-A- 2 060 485**
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DescriptionTECHNICAL FIELD

5 This invention is in the field of liquid automatic dishwashing compositions. More specifically, the invention relates to concentrated compositions containing non-phosphate builders, enzymes, and a potassium/sodium weight ratio of at least 0.01.

BACKGROUND OF THE INVENTION

10 Because of their convenience, dispensing characteristics and aesthetics, liquid and/or gel automatic dishwashing detergent compositions are a popular alternative to granular compositions among consumers. However, liquid and/or gel formulations often do not deliver the same effective cleaning, spotting and filming performance as a granular composition.

15 To clean effectively, conventional liquid/gel and granular automatic dishwashing detergents contain chlorine bleach, phosphate builders and have high alkalinity (i.e. silicate, carbonate and caustic). See, for example, U.S. Patents 4,116,849, Leikhim, issued September 26, 1978, 5,064,553, Dixit et al, issued November 12, 1991 and 4,917,812, Cilley, issued April 17, 1990. Incorporation of chlorine bleaches requires special processing, storage steps, and the use of chlorine bleach stable raw materials (which are mostly inorganic in nature). Automatic detergent compositions have been disclosed which use enzymes in place of chlorine bleach, for example, U.S. Patents 4,162,987, Maguire et al, issued July 31, 1979, 4,101,457, Place et al, issued July 18, 1978 and 5,075,027, Dixit et al, issued December 24, 1991.

20 It has recently been found that a viscoelastic, thixotropic liquid automatic dishwashing detergent can be formed which has superior performance to conventional liquid/gel products and comparable performance to granular products. Surprisingly, a low alkaline product pH (between 7 and 11) liquid composition which is substantially free of chlorine, and silicate, exhibits enhanced cleaning, spotting, and filming ability. The cleaning benefit is achieved via the presence of enzymes, and surfactant and/or builder in the composition. Removal of chlorine bleach and a lower product pH also results in a composition which is safer to dishwasher articles (i.e. china, silverware, glass).

25 Because of increasing environmental concerns, there is a movement away from phosphated compositions and excessive packaging materials. In order to maintain and achieve superior product performance without phosphate builders, more costly raw materials are required (e.g. enzymes and surfactants and new organic builders). Compaction or concentration of the formula composition has become a common means to help offset this economic upcharge, while simultaneously reducing solid waste.

30 However, the move from conventional formulations to concentrated formulas is not a simple matter of adding more active ingredients to conventional detergent formulations. This is especially true in the case of liquids where solubility of the ingredients is a limiting factor. It has now been found that a concentrated liquid automatic dishwashing detergent composition containing enzymes and non-phosphate builder(s) requires a potassium/sodium weight ratio of at least 0.01, preferably, between 0.01 and 10, in order to maintain long term product stability.

SUMMARY OF THE INVENTION

40 The composition of this invention is a concentrated viscoelastic, thixotropic, liquid automatic dishwashing detergent composition comprising, by weight:

- 45 (a) from 5% to 50% of a non-phosphate detergent builder selected from the group consisting of water-soluble, alkali metal, ammonium or substituted ammonium carbonates, bicarbonates, borates, polyhydroxysulfonates, polyacetates, carboxylates, polycarboxylates and mixtures thereof,
- (b) from 0.0001% to 5% of active deterative enzyme or enzymes;
- (c) from 0.1% to 10% of a viscoelastic, thixotropic thickener;
- 50 (d) sufficient pH adjusting agent to provide said composition with a product pH between about 7 and about 11; and
- (e) from 0.001% to 20% of an enzyme stabilizing system selected from the group consisting of calcium ion, propylene glycol, short chain carboxylic acid having a chain length at one carbon atom, polyhydroxyl compounds, boric acid, boronic acid, peptide aldehyde and mixtures thereof; and
- 55 (f) water, wherein the aqueous phase includes both potassium and sodium ions at a K/Na weight ratio of at least 0.01;

wherein said composition is substantially free of chlorine bleach, silicate, and phosphate.

A particularly preferred embodiment of this invention is a gel automatic dishwashing detergent composition further

comprising an organic dispersant, a detergent surfactant and/or a chlorine scavenger.

DETAILED DESCRIPTION OF THE INVENTION

The present invention encompasses viscoelastic, thixotropic, liquid automatic detergent compositions which exhibit enhanced performance in the absence of chlorine bleach, silicate, and phosphate. These detergent compositions contain the following components by weight of the composition:

- (a) from 5% to 50% of a non-phosphate detergent builder selected from the group consisting of water-soluble, alkali metal, ammonium or substituted ammonium carbonates, bicarbonates, borates, polyhydroxysulfonates, polyacetates, carboxylates, polycarboxylates and mixtures thereof;
- (b) from 0.0001% to 5% of active detergent enzyme or enzymes;
- (c) from 0.1% to 10% of a viscoelastic, thixotropic thickener;
- (d) sufficient pH adjusting agent to provide said composition with a product pH between about 7 and about 11; and
- (e) from 0.001% to 20% of an enzyme stabilizing system selected from the group consisting of calcium ion, propylene glycol, short chain carboxylic acid having a chain length at one carbon atom, polyhydroxyl compounds, boric acid, boronic acid having a chain length at one carbon atom, peptide aldehyde and mixtures thereof; and
- (f) water, wherein the aqueous phase includes both potassium and sodium ions at a K/Na weight ratio of at least 0.01;

wherein said composition is substantially free of chlorine bleach, silicate, and phosphate.

Various other optional ingredients, such as fatty acids, oxygen bleaches, perfumes, dyes, suds control agents, and organic dispersants, can be added to provide additional performance, product stability, and aesthetic benefits.

These components result in a viscoelastic, thixotropic, liquid automatic dishwashing detergent composition which exhibits cleaning, spotting and filming performance superior to conventional liquid automatic dishwashing detergent compositions, and equal to or better than conventional granular automatic dishwashing detergent compositions. A particularly preferred composition is a gel formulation.

The term thixotropic means the material exhibits a decrease in viscosity with increasing shear stress. In other words, it exhibits high viscosity when subjected to low shear stress and lower viscosity when subjected to higher shear stress. A viscoelastic liquid exhibits a steady state flow behavior after a constant shear stress has been applied for a sufficiently long period of time.

The term "substantially free" is defined herein to pertain to substances in the invention that are not intentionally added, but could be present as trace impurities in other raw material feedstocks. Preferably, the compositions of the present invention comprises less than 0.5% form of phosphorous, and less than 0.2% silicate. No level of chlorine bleach species is acceptable; however, if present chlorine scavengers discussed herein can be added to the composition.

All percentages herein refer to weight percent of active material in the final composition unless otherwise noted.

Detergency Builder

The detergency builders used can be any of the non-phosphate detergency builders known in the art, which include the various water-soluble, alkali metal, ammonium or substituted ammonium carbonates, bicarbonates, borates, polyhydroxysulfonates, polyacetates, carboxylates (e.g. citrates), and polycarboxylates. Preferred are the alkali metal, especially sodium and potassium, salts of the above and mixtures thereof.

The amount of builder is from 5% to 50%, preferably from 8% to 40%, most preferably from 10% to 30% by weight of the automatic dishwashing detergent composition.

Examples of non-phosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, and sesquicarbonate.

Water-soluble, non-phosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates (e.g. citrates), polycarboxylates and polyhydroxysulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxy methyloxysuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Preferred detergency builders have the ability to remove metal ions other than alkali metal ions from washing solutions by sequestration, which as defined herein includes chelation, or by precipitation reactions. Some of the above-described detergency builders additionally serve as buffering agents (pH adjusting), and/or chlorine scavengers.

Particularly preferred automatic dishwashing detergent compositions of the invention contain, by weight of the automatic dishwashing detergent composition, from 5% to 50%, preferably from 8% to 30%, most preferably from 10%

to 30%, of carbonate, citrate, and mixtures thereof.

The compositions of this invention must include sufficient amounts of potassium and sodium ions to provide a finished product K/Na weight ratio of at least 0.01, preferably between 0.01 and 10, more preferably between 0.1 and 1.0, even more preferably between 0.1 and 0.8, most preferably between 0.1 and 0.5. The potassium and sodium ions can be incorporated into the composition from the alkali metal cation of the detergent builder salt(s), or alkali metal hydroxide(s), or as the alkali metal cation of any other component of the composition. In determining the total finished product K/Na weight ratio, all of these sources should be taken into consideration.

Not to be bound by theory, it is believed that increasing the water solubility of the detergent salts is the means to achieve high builder levels while maintaining long term stability. In the compact formulations of the present invention, there is a reduction in the amount of available water. Therefore, it becomes more difficult to solubilize the builder salts, especially when only sodium salts are used. It has been found that the use of all sodium builder salts in matrices similar to this invention results in excessive crystal growth/precipitation when the product is to long term storage (greater than one month) and/or harsh conditions. It has been found that a stable composition can be formed by incorporating potassium ions into compositions of the present invention.

The finished product K/Na weight ratio is directly proportional to the weight percent of detergent components/salts incorporated in the composition. A higher weight percent of detergent components in the composition requires a higher finished product K/Na weight ratio to achieve acceptable finished product stability. For example, in composition of the present invention containing citrate and carbonate builders, the K/Na ratio should be between 0.01 and 0.20 for builder levels between 5% and 10%; between 0.05 and 1.50 for builder levels between 10% and 30%; and between 0.6 and 10.0 for builder levels between 30% and 50%.

Detergent Enzyme

The compositions of this invention can contain from 0.0001% to 5%, more preferably from 0.001% to 1%, most preferably from 0.005% to 0.5%, by weight, of active detergent enzyme. Weight percent of "active detergent enzyme" is defined by the weight percent of the enzyme present in the composition - it does not include the weight percent of other materials commonly included in commercial enzyme feedstocks (e.g. solvents, stabilizers, residuals).

The preferred detergent enzyme is selected from the group consisting of protease, amylase, lipase and mixtures thereof. Most preferred are protease or amylase or mixtures thereof.

The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or nonpurified forms of this enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants. Particularly preferred is bacterial serine proteolytic enzyme obtained from Bacillus, Bacillus subtilis and/or Bacillus licheniformis.

Suitable proteolytic enzymes include AlcaseR, EsperaseR, DurazymR, SavinaseR (preferred); MaxataseR MaxacalR (preferred), and MaxapemR 15 (protein engineered Maxacal), PurafectR (preferred) and subtilisin BPN and BPN'; which are commercially available. Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein and in PCT Application Number WO 91/02792, Wilson et al, published March 7, 1991 which is called "BLAP" herein. Preferred proteolytic enzymes, then, are selected from the group consisting of SavinaseR, AlcalaseR, EsperaseR, MaxacalR, PurafectR, BPN', Protease A and Protease B, and mixtures thereof. SavinaseR or "Protease B" is most preferred.

Suitable lipases for use herein include those of bacterial, animal, and fungal origin, including those from chemically or genetically modified mutants.

Suitable bacterial lipases include those produced by Pseudomonas, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase produced from the microorganism Pseudomonas fluorescens IAM 1057. This lipase and a method for its purification have been described in Japanese Patent Application 53-20487, laid open on February 24, 1978. This lipase is available under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Such lipases should show a positive immunological cross reaction with the Amano-P antibody, using the standard and well-known immunodiffusion procedure according to Ouchterlony (Acta. Med. Scan., 133, pages 76-79 (1950)). These lipases, and a method for their immunological cross-reaction with Amano-P, are also described in U.S. Patent 4,707,291, Thom et al., issued November 17, 1987. Typical examples thereof are the Amano-P lipase, the lipase ex Pseudomonas fragi FERM P 1339 (available under the trade name Amano-B), lipase ex Pseudomonas nitroreducens var. lipolyticum FERM P 1338 (available under the trade name Amano-CES), lipases ex Chromobacter viscosum var. lipolyticum NRRLb 3673, and further Chromobacter viscosum lipases, and lipases ex Pseudomonas gladioli. A preferred

lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272. Other lipases of interest are Amano AKG and Bacillis Sp lipase (e.g. Solvay enzymes).

Other lipases which are of interest where they are compatible with the composition are those described in EP A 0 339 681, published November 28, 1990, EP A 0 385 401, published September 5, 1990, EO A 0 218 272, published April 15, 1987, and PCT/DK 88/00177, published May 18, 1989.

Suitable funzal lipases include those produced by Humicola lanuginosa and Thermomyces lanuginosus. Most preferred is lipase obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryzae as described in European Patent Application 0 258 068, commercially available under the trade name LipolaseR from Novo-Nordisk.

Any amylase suitable for use in a dishwashing detergent composition can be used in these compositions. Amylases include for example, α -amylases obtained from a special strain of B. licheniformis, described in more detail in British Patent Specification No. 1,296,839. Amylolytic enzymes include, for example, Rapidase™, Maxamyl™, Termamyl™ and BAN™.

Enzyme Stabilizing System

The preferred compositions herein comprise from 0.001% to 20%, preferably from 0.01% to 15%, most preferably from 0.5% to 12%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the enzyme of the present invention. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid having a chain length of one carbon atom boronic acid, Polyhydroxyl compounds, peptide aldehydes, and mixtures thereof. The level of calcium ion should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, etc., in the composition. Any water-soluble calcium salt can be used as the source of calcium ion, including calcium chloride, calcium formate, and calcium acetate. A small amount of calcium ion, from 0.05 to 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme and formula water. Calcium ions can be used with boric acid or a suitable salt of boric acid, described herein below, in a composition with a product pH between 7 and 9. However, calcium ions and the salt of boric acid can associate to form calcium borate which is insoluble in cold water and under certain product conditions can be insoluble above about pH 9. This precipitate can lead to phase instability, decrease in effective enzyme stabilization and undesired product aesthetics. Therefore, a sufficient amount of calcium ion and boric acid or the salt of boric acid should be used to achieve enzyme stability without affecting phase stability, enzyme stability, or aesthetics. From 0% to 1%, more preferably from 0.05% to 0.45% of calcium formate is preferred.

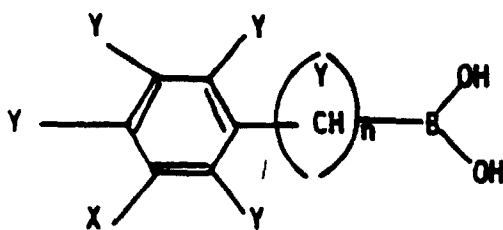
Other suitable enzyme stabilizing systems comprise polyols containing only carbon, hydrogen and oxygen atoms. They preferably contain from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups. Examples include propylene glycol (especially 1,2-propanediol, which is preferred), 1,2- butanediol, ethylene glycol, glycerol, sorbitol, mannitol, and glucose. The polyol generally represents from 0.001% to 20%, preferably from 1.5% to 8%, by weight of the composition. Preferably, the weight ratio of polyol to a boric acid added is at least 1, most preferably at least about 1.3.

The compositions can also contain the water-soluble short chain carboxylates having a chain length of one carbon atom described in U.S. Patent 4,318,818, Letton et al., issued March 9, 1982. The formates are preferred and can be used at levels from 0% to 5%, preferably from 0.075% to 2.5%, most from 0.1% to 1.5%, by weight. Sodium formate is preferred.

Another stabilizing system comprises from 0.05% to 7%, preferably from 0.1% to 5%, by weight of boric acid. The boric acid may be, but is not, formed by a compound capable of forming boric acid in the composition. Boric acid is preferred, although other compounds such as boric oxide, borax, and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable.

Still another enzyme stabilizing system includes polyhydroxyl compounds, such as sugar alcohols, monosaccharides and disaccharides as disclosed in the specification of German Pat. No. 2,038,103, water-soluble sodium or potassium salts and water-soluble hydroxy alcohols, as disclosed in U.S. Published Patent Application B-458,819, Weber, published April 13, 1976; diamines and polyamines, as disclosed in German Pat. No. 2,058,826; amino acids, as disclosed in German Pat. No. 2,060,485; and reducing agents, as disclosed in Japanese Pat. No. 72-20235. Further, in order to enhance its storage stability, the enzyme mixture may be incorporated into the detergent composition in a coated, encapsulated, agglomerated, prilled, or noodled form in accordance with, e.g., U.S. Patent 4,162,987, Maguire et al, issued July 31, 1979.

Substituted boric acids (e.g. phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid. A particularly preferred boronic acid is an aryl boronic acid of the structure:



where x is selected from C₁-C₆ alkyl, substituted C₁-C₆ alkyl, aryl, substituted aryl, hydroxyl, hydroxyl derivative, amine C₁-C₆ alkylated amine, amine derivative, halogen, nitro, thiol, thio derivative, aldehyde, acid, acid salt, ester, sulfonate or phosphonate; each Y is independently selected from hydrogen, C₁-C₆ alkyl, substituted C₁-C₆ alkyl, aryl, substituted aryl, hydroxyl, hydroxyl derivative, halogen, amine, alkylated amine, amine derivative, nitro, thiol, thiol derivative, aldehyde, acid, ester, or sulfonate; and n is 0 to 4.

Yet another suitable stabilizing system includes a peptide aldehyde comprising from 2 to 50 amino acids, or mixtures thereof. As used herein, the term peptide aldehydes refers to compounds comprising a peptidic chain wherein the C-terminal end of said chain is converted from a carboxylic group to an aldehyde group. Peptide aldehydes are known per se and have been described as well as processes for their manufacture, for instance in US 5,015,627, EP 185 930 and DE 32 00 812. Preferred peptide aldehydes for use herein comprise from 2 to 6 amino acids, most preferably 3 to 4.

Thickening Agent

The viscoelastic, thixotropic thickening agent in the compositions of the present invention is from 0.1% to 10%, preferably from 0.25% to 8%, most preferably from 0.5% to 5%, by weight of the detergent composition. Preferably, the viscoelastic, thixotropic thickening agent is free of any enzymatically reactive species. Without being bound by theory, it is believed that the enzyme(s) present in the automatic detergent composition could degrade the thickening agent which contains such species, resulting in a rheologically unstable product.

Preferably the thickening agent is a polymer with a molecular weight at least 500,000, preferably from 500,000 to 10,000,000. The polymeric thickening agent can be, but is not limited to, a cross-linked polycarboxylate polymer.

The preferred cross-linked polycarboxylate polymer is preferably a carboxyvinyl polymer. Such compounds are disclosed in U.S. Patent 2,798,053, issued on July 2, 1957, to Brown. Methods for making carboxyvinyl polymers are also disclosed in Brown. Carboxyvinyl polymers are substantially insoluble in liquid, volatile organic hydrocarbons and are dimensionally stable on exposure to air.

Preferred polyhydric alcohols used to produce carboxyvinyl polymers include polyols selected from the class consisting of oligosaccharides, reduced derivatives thereof in which the carbonyl group is converted to an alcohol group, a pentaerythritol; most preferred is sucrose or pentaerythritol. It is preferred that the hydroxyl groups of the modified polyol be etherified with allyl groups, the polyol having at least two allyl ether groups per polyol molecule. When the polyol is sucrose, it is preferred that the sucrose have at least about five allyl ether groups per sucrose molecule. It is preferred that the polyether of the polyol comprise from 0.1% to about 4% of the total monomers, more preferably from 0.2% to 2.5%.

Preferred monomeric olefinically unsaturated carboxylic acids for use in producing carboxyvinyl polymers used herein include monomeric, polymerizable, alpha-beta monoolefinically unsaturated lower aliphatic carboxylic acids; more preferred are monomeric monoolefinic acrylic acids of the structure

R



where R is a substituent selected from the group consisting of hydrogen and lower alkyl groups; for example, acrylic acid.

Various carboxyvinyl polymers, homopolymers and copolymers are commercially available from B.F. Goodrich Company, New York, N.Y., under the trade name Carbopol®. These polymers are also known as carbomers or polyacrylic acids. Carboxyvinyl polymers useful in formulations of the present invention include Carbopol 910 having a molecular weight of about 750,000, Carbopol 941 having a molecular weight of 1,250,000, and Carbopols 934 and

940 having molecular weights of 3,000,000 and 4,000,000, respectively. More preferred are the series of Carbopols which use ethyl acetate and cyclohexane in the manufacturing process, for example, Carbopol 981, 2984, 980, and 1382.

Preferred polycarboxylate polymers of the invention are non-linear, water-dispersible, polyacrylic acid cross-linked with a polyalkenyl polyether and having a molecular weight of at least 750,000, preferably from 750,000 to 4,000,000.

Highly preferred examples of these polycarboxylate polymers for use in the present invention are Sokalan PHC-25R, a polyacrylic acid available from BASF Corporation, the Carbopol series resins available from B.F. Goodrich, and the Polygel series available from 3-V Chemical Corporation. Mixtures of polycarboxylate polymers as herein described may also be used.

The polycarboxylate polymer thickening agent can be used alone or with inorganic clays (e.g. aluminum silicate, bentonite, fumed silica). The preferred clay thickening agent can be either naturally occurring or synthetic. A preferred synthetic clay is the one disclosed in U.S. Patent 3,843,598. Naturally occurring clays include some smectite and attapulgite clays as disclosed in U.S. Patent 4,824,590.

Other types of thickeners which can be used in this composition include natural gums, such as xanthan gum, locust bean gum and guar gum. Semi-synthetic thickeners such as the cellulosic type thickeners: hydroxyethyl and hydroxymethyl cellulose (ETHOCEL and METHOCEL available from Dow Chemical) can also be used. Mixtures of polymeric thickening agents, semi-synthetic, and natural thickeners herein described may also be used.

In the preferred viscoelastic thixotropic liquid automatic dishwashing detergent composition, the polycarboxylate polymer thickening agent provides an apparent viscosity at high shear of greater than 250 centipoise and an apparent yield value of from 40 to 800, and most preferably from 60 to 600, dynes/cm² to the composition.

Viscosity is a measure of the internal resistance to flow-exhibited by a fluid in terms of the ratio of the shear stress to the shear rate. The yield value is an indication of the shear stress at which the gel strength is exceeded and flow is initiated. Yield value can be measured herein with a Brookfield RVT model viscometer with a T-bar B spindle at about 77°F (25°C) utilizing a Helipath drive during associated readings. The system is set to 0.5 rpm and a torque reading is taken for the composition to be tested after 30 seconds or after the system is stable. The system is stopped and the rpm is reset to 1.0 rpm. A torque-reading is taken for the same composition after 30 seconds or after the system is stable. Apparent viscosities are calculated from the torque readings using factors provided with the Brookfield viscometer. An apparent Brookfield yield value is then calculated as: Brookfield Yield Value = (apparent viscosity at 0.5 rpm - apparent viscosity at 1 rpm)/100. This is the common method of calculation, published in Carbopol literature from the B. F. Goodrich Company and in other published references. In the cases of most of the formulations quoted herein, this apparent yield value is approximately four times higher than yield values calculated from shear rate and shear stress measurements in more rigorous rheological equipment. Apparent viscosities at high shear are determined with a Brookfield RVT viscometer with spindle #6 at 100 rpm, reading the torque at 30 seconds.

A preferred method herein for measuring viscosity and yield value is with a Contraves Rheomat 115 viscometer which utilizes a Rheoscan 100 controller, a DIN 145 spindle and cup at 25°C. For viscosity measurements, the shear rate is increased from 0 to 150 sec⁻¹ over a 30 second time period. The viscosity, measured in centipoise, is taken at a shear rate of 150 sec⁻¹. The shear rate for yield value measurements is increased linearly from 0 to 0.4 sec⁻¹ over a period of 500 seconds after an initial 5 minute rest period.

pH Adjusting Agent

In the instant compositions, one or more buffering agents can be included which are capable of maintaining the pH of the compositions within the desired alkaline range. The pH of the undiluted composition ("as is") is determined at room temperature (20°C) with a pH meter. It is in the low alkaline pH range that optimum performance and stability of the enzyme are realized, and it is also within this pH range wherein optimum compositional, chemical, and physical stability are achieved.

Maintenance of the composition pH between 7 and 11, preferably between 8 and 10.5, minimizes undesirable degradation of the active enzymes. Maintenance of this particular pH range also maximizes the soil and stain removal properties and prevents spotting and filming during utilization of the present compositions.

The pH adjusting agents are generally present in a level from 0% to 50%, preferably from 8% to 40% by weight of the detergent composition.

Any compatible material or mixture of materials which has the effect of maintaining the composition pH within the pH range of 7 to 11, preferably 8 to 10.5, most preferably 9 to 10.5, can be utilized as the pH adjusting agent in the instant invention. Such agents can include, for example, various water-soluble, inorganic salts such as the carbonates, bicarbonates, sesquicarbonates, tetraborates, hydroxides, and mixtures thereof. Silicates are not included because of their high alkaline buffering properties.

Examples of preferred materials which can be used either alone or in combination as the pH adjusting agent herein include sodium carbonate, sodium bicarbonate, potassium carbonate, sodium sesquicarbonate, organic amines and

their salts such as monoethanol amine (MEA), anhydrous sodium tetraborate, sodium tetraborate pentahydrate, potassium hydroxide, sodium hydroxide, and sodium tetraborate decahydrate. Combinations of these pH adjusting agents, which include both the sodium and potassium salts, may be used. As set forth herein, the compositions of the present invention comprise sufficient amount of both potassium and sodium ions. The pH adjusting can be a source for these ions.

Detergent Surfactants

The compositions of this invention can contain from 0% to 20%, preferably from 0.1% to 15%, more from 1% to 10% of a detergent surfactant which preferably results in a low foaming detergent composition. Preferably the detergent surfactant is low foaming or which in combination with other components (i.e. suds suppressors) is low foaming. Most preferably the surfactant is a low foaming nonionic surfactant.

Because the composition is chlorine bleach free, there is no requirement that the surfactant be chlorine bleach stable. However, since enzymes are an essential ingredient of the invention, the surfactant employed is preferably enzyme stable (enzyme compatible) and free of enzymatically reactive species. For example, when proteases and amylases are employed, the surfactant should be free of peptide or glycosidic bonds. In addition, because the composition is phosphate free, compounds containing phosphorous should be avoided.

Desirable detergent surfactants include nonionic, anionic, amphoteric and zwitterionic detergent surfactants, and mixtures thereof.

Examples of nonionic surfactants include:

(1) The condensation product of 1 mole of a saturated or unsaturated, straight or branched chain, alcohol or fatty acid containing from 10 to 20 carbon atoms with from about 4 to 40 moles of ethylene oxide. Particularly preferred is the condensation product of a fatty alcohol containing from 17 to 19 carbon atoms, with from 6 to 15 moles, preferably 7 to 12 moles, most preferably 9 moles, of ethylene oxide provides superior spotting and filming performance. More particularly, it is desirable that the fatty alcohol contain 18 carbon atoms and be condensed with from 7.5 to 12, preferably 9 moles of oxide. These various specific C₁₇-C₁₉ ethoxylates give extremely good performance even at lower levels (e.g., 2.5%-3%). At the higher levels (less than 5%), they are sufficiently low sudsing, especially when capped with a low molecular weight (C₁₋₅) acid or alcohol moiety, so as to minimize or eliminate the need for a suds-suppressing agent. Suds-suppressing agents in general tend to act as a load on the composition and to hurt long term spotting and filming characteristics.

(2) Polyethylene glycols or polypropylene glycols having molecular weight of from 1,400 to 30,000, e.g., 20,000; 9,500; 7,500; 7,500; 6,000; 4,500; 3,400; and 1,450. All of these materials are wax-like solids which melt between 110°F (43°C) and 200°F (93°C).

(3) The condensation products of 1 mole of alkyl phenol wherein the alkyl chain contains from 8 to 18 carbon atoms and from 4 to 50 moles of ethylene oxide.

(4) Polyoxypropylene, polyoxyethylene condensates having the formula HO(C₂H₆O)_x(C₃H₆O)_xH or HO(C₃H₆O)_y(C₂H₄O)_x(C₃H₆O)_yH where total y equals at least 15 and total (C₂H₄O) equals 20% to 90% of the total weight of the compound and the molecular weight is from 2,000 to 10,000, preferably from 3,000 to 6,000. These materials are, for example, the PLURONICSR which are well known in the art.

(5) the compounds of (1) and (4) which are capped with propylene oxide, butylene oxide and/or short chain alcohols and/or short chain fatty acids, e.g., those containing from 1 to about 5 carbon atoms, and mixtures thereof.

Useful surfactants in detergent compositions are those having the formula RO-(C₂H₄O)_xR¹ wherein R is an alkyl or alkylene group containing from 17 to 19 carbon atoms, x is a number from 6 to 15, preferably from 7 to 12, and R¹ is selected from the group consisting of: preferably, hydrogen, C₁₋₅ alkyl groups, C₂₋₅ acyl groups and groups having the formula -(C_yH_{2y}O)_nH wherein y is 3 or 4 and n is a number from one to about 4.

Particularly suitable surfactants are the low-sudsing compounds of (4), the other compounds of (5), and the C₁₇-C₁₉ materials of (1) which have a narrow ethoxy distribution. Certain of the block co-polymer surfactant compounds designated PLURONIC, PLURAFACR and TETRONICR by the BASF Corp., Parsippany, N.J. are suitable as the surfactant for use herein. A particularly preferred embodiment contains a polyoxypropylene, polyoxyethylene block polymer blend comprising 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 mole of propylene oxide; and 25%, by weight of the blend, of a block co-polymer of polyoxyethylene and polyoxypropylene, initiated with tri-methylol propane, containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylol propane.

Additional nonionic type surfactants which may be employed have melting points at or above ambient temperatures, such as octyldimethylamine N-oxide dihydrate, decyldimethylamine N-oxide dihydrate, C8-C12 N-methyl-glucamides and the like. Such surfactants may advantageously be blended in the instant compositions with short-chain anionic

surfactants, such as sodium octyl sulfate and similar alkyl sulfates, though short-chain sulfonates such as sodium cumene sulfonate could also be used.

In addition to the above mentioned surfactants, other suitable surfactants for detergent compositions can be found in the disclosures of U.S. Patents 3,544,473, 3,630,923, 3,88,781 and 4,001,132.

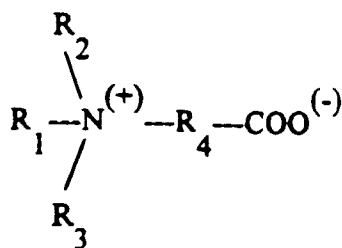
Anionic surfactants which are suitable for the compositions of the present invention include, but are not limited to, water soluble secondary alcohol sulfates, and alkyl sulfates and/or sulfonates, containing from 6 to 18 carbon atoms.

Natural fatty alcohols include those produced by reducing the glycerides of naturally occurring fats and oils. Fatty alcohols can be produced synthetically, for example, by the Oxo process. Examples of suitable alcohols which can be employed in alkyl sulfate manufacture include nonyl, undecyl, decyl, lauryl, tridecyl, myristyl, pentadecyl, palmityl and stearyl alcohols and the mixtures of fatty alcohols derived by reducing the glycerides of tallow and coconut oil.

Specific examples of alkyl sulfate salts which can be employed in the instant detergent compositions include sodium lauryl alkyl sulfate, sodium stearyl alkyl sulfate, sodium palmityl alkyl sulfate, sodium decyl sulfate, sodium myristyl alkyl sulfate, potassium lauryl alkyl sulfate, potassium stearyl alkyl sulfate, potassium decyl sulfate, potassium palmityl alkyl sulfate, potassium myristyl alkyl sulfate, sodium dodecyl sulfate, potassium dodecyl sulfate, potassium tallow alkyl sulfate, sodium tallow alkyl sulfate, sodium coconut alkyl sulfate, magnesium coconut alkyl sulfate, calcium coconut alkyl sulfate, potassium coconut alkyl sulfate and mixtures thereof. Highly preferred alkyl sulfates are sodium coconut alkyl sulfate, potassium coconut alkyl sulfate, potassium lauryl alkyl sulfate and sodium lauryl alkyl sulfate.

A preferred sulfonated anionic surfactant is the alkali metal salt of secondary alkane sulfonates, an example of which is the Hostapur SAS from Hoechst Celanese.

Another class of surfactants operable in the present invention are the water-soluble betaine surfactants. These materials have the general formula:



wherein R_1 is an alkyl group containing from about 8 to 22 carbon atoms; R_2 and R_3 are each lower alkyl groups containing from about 1 to 5 carbon atoms, and R_4 is an alkylene group selected from the group consisting of methylene, propylene, butylene and pentylene. (Propionate betaines decompose in aqueous solution and hence are not included in the instant compositions).

Examples of suitable betaine compounds of this type include dodecyldimethylammonium acetate, tetradecyldimethylammonium acetate, hexadecyldimethylammonium acetate, alkyl dimethylammonium acetate wherein the alkyl group averages 14.8 carbon atoms in length, dodecyldimethylammonium butanoate, tetradecyldimethylammonium butanoate, hexadecyldimethylammonium butanoate, dodecyl dimethylammonium hexanoate, hexadecyldimethylammonium hexanoate, tetradecyldiethylammonium pentanoate and tetradecyldipropylammonium pentanoate. Especially preferred betaine surfactants include dodecyldimethylammonium acetate, dodecyldimethylammonium hexanoate, hexadecyldimethylammonium acetate, and hexadecyldimethylammonium hexanoate.

Other surfactants include amine oxides and sulfoxides. However, such surfactants are usually high sudsing. A disclosure of surfactants can be found in published British Patent Application 2,116,199A; U.S. Patent 4,005,027, Hartman; U.S. Patent 4,116,851, Rupe et al; U.S. Patent 3,985,668, Hartman; U.S. Patent 4,271,030, Brierley et al; and U.S. Patent 4,116,849, Leikhim.

Still other preferred anionic surfactants include the linear or branched alkali metal mono- and/or di-(C_{8-14}) alkyl diphenyl oxide mono- and/or disulfonates, commercially available under the trade name DOWFAXR 3B-2 (sodium n-decyl diphenyloxide disulfonate) and DOWFAXR 2A-1. These and similar surfactants are disclosed in published U.K. Patent Applications 2,163,447A; 2,163,448A; and 2,164,350A.

Chlorine Scavengers

In addition to the above listed enzyme stabilizers, from 0 to 10%, preferably from 0.01% to 6% by weight, of chlorine bleach scavengers can be added to prevent chlorine bleach species present in many water supplies from attacking and deactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from 0.5 ppm to 1.75 ppm, the available chlorine in the total volume of water that comes in contact

with the enzyme during dishwashing is usually large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions for compositions of the present invention with a pH less than 8 are salts containing ammonium cations. These can be selected from the group consisting of reducing materials like sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc., antioxidants like carbamate, ascorbate. Other conventional scavenging anions like sulfate, bisulfate, carbonate, bicarbonate, percarbonate, nitrate, chloride, borate, sodium perborate tetrahydrate, sodium perborate monohydrate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof and monoethanolamine (MEA), and mixtures thereof, preferably monoethanolamine, can also be used. Some of the above-described chlorine scavengers additionally serve as, detergency builders, pH adjusting agents, and/or bleaching agents.

Organic Dispersant

The present compositions can contain an organic dispersant which overcomes the problem of unsightly films and spots which form on china and especially on glassware due to calcium or magnesium hardness induced precipitation of the builders and/or pH adjusting agents (e.g. especially carbonate).

The organic dispersants herein can be used at levels of 0 to 40% typically from 0.5% to 30%, most preferably from 1% to 20% of the automatic dishwashing composition. Such organic dispersants are preferably water-soluble sodium polycarboxylates. ("Polycarboxylate" dispersant herein generally contain truly polymeric numbers of carboxylate groups, e.g., 8 or more, as distinct from carboxylate builders, sometimes called "polycarboxylates" in the art when, in fact, they have relatively low numbers of carboxylate groups such as four per molecule.) The organic dispersants are known for their ability to disperse or suspend calcium and magnesium "hardness", e.g., carbonate salts. Crystal growth inhibition, e.g., of Ca/Mg carbonates, is another useful function of such materials. Preferably, such organic dispersants are polyacrylates or acrylate-containing copolymers. "Polymeric Dispersing Agents, SOKALAN", a printed publication of BASF Aktiengesellschaft, D-6700 Ludwigshafen, Germany, describes organic dispersants useful herein. Preferred dispersants herein described include, but are not limited to sodium polyacrylate having a nominal molecular weight of 4500, obtainable from Rohm & Haas under the tradename ACUSOLR (e.g. ACUSOLR 445N), or acrylate/maleate copolymers such as are available under the tradename SOKALANR, from BASF Corp. These polyanionic materials are, as noted, usually available as viscous aqueous solutions, often having dispersant concentrations of 30-50%. The organic dispersant is most commonly fully neutralized; e.g., as the sodium salt form.

While the foregoing encompasses preferred organic dispersants for use herein, it will be appreciated that other oligomers and polymers of the general polycarboxylate type can be used, according to the desires of the formulator. Suitable polymers are generally low molecular weight and at least partially neutralized in the form of their alkali metal, ammonium or other conventional cation salts. The alkali metal, especially sodium salts, are most preferred. While the molecular weight of such dispersants can vary over a wide range, it preferably is from 1,000 to 500,000, more preferably is from 2,000 to 250,000, and most preferably is from 3,000 to 100,000. Nonlimiting examples of such materials are as follows.

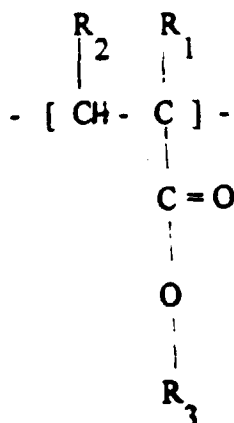
For example, other suitable organic dispersants include those disclosed in U.S. Patent 3,308,067 issued March 7, 1967, to Diehl. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence of monomeric segments containing no carboxylate radicals such as vinyl-methyl ether, styrene, ethylene, etc. is suitable, preferably when such segments do not constitute more than 40% by weight of the polymer.

Other suitable organic dispersants for use herein are copolymers of acrylamide and acrylate having a molecular weight of from 3,000 to 100,000, preferably from 4,000 to 20,000, and an acrylamide content of less than 50%, preferably less than 20%, by weight of the polymer. Most preferably, the polymer has a molecular weight of from about 4,000 to 10,000 and an acrylamide content of from 1% to 15%, by weight of the polymer.

Still other useful organic dispersants include acrylate/ maleate or acrylate/fumarate copolymers with an average molecular weight in acid form of from 2,000 to 80,000 and a ratio of acrylate to maleate or fumarate segments of from 30:1 to 2:1. Other such suitable copolymers based on a mixture of unsaturated mono- and dicarboxylate monomers are disclosed in European Patent Application No. 66,915, published December 15, 1982. Yet other organic dispersants are useful herein, as illustrated by water-soluble oxidized carbohydrates, e.g., oxidized starches prepared by art-disclosed methods.

A particularly preferred embodiment of the present invention can contain from 0% to 40%, preferably from 1% to 30%, most preferably from 1% to 20%, by weight of the automatic dishwashing detergent composition, of low molecular weight modified polyacrylate copolymers.

The term modified polyacrylate is defined as a copolymer which contains as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula:



wherein at least one of the substituents R_1 , R_2 or R_3 , preferably R_1 or R_2 is a 1 to 4 carbon alkyl or hydroxyalkyl group, R_1 or R_2 can be a hydrogen and R_3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_1 is methyl, R_2 is hydrogen and R_3 is sodium.

The low molecular weight modified polyacrylate preferably has a molecular weight of less than 15,000, preferably from 500 to 10,000, most preferably from 1,000 to 5,000. The most preferred polyacrylate copolymer has a molecular weight of 3500 and is 70% by weight acrylic acid and 30% by weight methyl acrylic acid.

Suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids as disclosed in U.S. Patent 4,530,766, and 5,084,535.

Other Optional Ingredients

Metal salts of long chain fatty acids and/or long chain hydroxy fatty acids have been found to be useful in automatic dishwashing detergent compositions to inhibit tarnishing caused by repeated exposure of sterling or silver-plate flatware to bleach-containing automatic dishwashing detergent compositions (U.S. Patent 4,859,358, Gabriel et al). By "long chain" is meant the higher aliphatic fatty acids or hydroxy fatty acids having from 6 to 24 carbon atoms, preferably from 8 to 22 carbon atoms, and most preferably from 10 to 20 carbon atoms and most preferably from 12 to 18, inclusive of the carbon atom of carboxyl group of the fatty acid, e.g., stearic acid, and hydroxy stearic acid. By "metal salts" of the long chain fatty acids and/or hydroxy fatty acids is meant both monovalent and polyvalent metal salts, particularly the sodium, potassium lithium, aluminum, and zinc salts, e.g., lithium salts of the fatty acids. Specific examples of this material are aluminum, potassium sodium, calcium and lithium stearate or hydroxy stearate, particularly preferred is aluminum tristearate. If the metal salts of long chain hydroxy fatty acids are incorporated into the automatic dishwashing detergent compositions of the present invention, this component generally comprises from 0% to 2%, preferably from 0.05% to 0.2% by weight of the composition.

An alkali metal salt of an amphoteric metal salt of an amphoteric metal anion (metalate), such as aluminate, can be added to provide additional structuring to the polycarboxylate polymer thickening agent. See U. S. Patent 4,941,988, Wise, issued July 17, 1990.

Compounds known, or which become known, for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. The compositions hereof will generally comprise from 0% to 5% of suds suppressor. Suitable suds suppressors are described in Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979), U.S. Patent 2,954,347, issued September 27, 1960 to St. John, U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al., and European Patent Application No. 89307851.9, published February 7, 1990, U.S. Patent 3,455,839, German Patent Application DOS 2,124,526, U.S. Patent 3,933,672, Bartolatta et al and U.S. Patent 4,652,392, Baginski. A commercially acceptable suds suppressor is LPKN, from Knapsack.

Suitable nonchlorine bleaches in the present compositions are solid, water-soluble peroxygen compounds in levels from 0 to 15%, preferably from 0.2% to 12% by weight of the composition. The peroxygen compound can be a preformed peroxyacid, an inorganic persalt or a combination of an inorganic per salt and an inorganic precursor (i.e. bleach activator).

Examples of suitable organic peroxyacids are disclosed in U.S. Patents 4,374,035, Bossu, issued Feb. 15, 1983; 4,681,592, Hardy et al, issued July 21, 1987; 4,634,551, Burns et al, issued Jan. 6, 1987; 4,686,063, Burns, issued Aug. 11, 1987; 4,606,838, Burns, issued Aug. 19, 1986; and 4,671,891, Hartman, issued June 9, 1987. Examples of compositions which contain perborate bleaches and activators therefore are disclosed in U.S. Patent 4,412,934, Chung and Spadini, issued Nov. 1, 1983; 4,536,314, Hardy et al, issued Aug. 20, 1985; 4,681,695, Divo, issued July 21, 1987;

and 4,539,120, Thompson et al, issued Sept. 3, 1985.

Preferred compositions of the invention contain peroxygen compounds such as perborates, persulfates, percarbonates, peroxydisulfates, crystalline peroxyhydrates and mixtures thereof.

Liquid detergent compositions can contain water and other solvents as carriers. These solvents include, but are not limited to, low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., propylene glycol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used.

Other solvents include the higher glycols, polyoxides, glycol ethers, propylene glycol ethers and tripropylene glycol ethers. Any water used in the composition should preferably be softened or deionized.

A wide variety of other ingredients useful in detergent compositions can be included in the compositions hereof, including other active ingredients, carriers, hydrotropes, draining promoting agents, processing aids, corrosion inhibitors, perfumes, dyes or pigments, etc.

If present, the above-described other optional materials generally are enzyme compatible and are dissolved, suspended, or emulsified in the present compositions.

Composition

Preferred viscoelastic, thixotropic, liquid automatic dishwashing detergent compositions hereof will preferably be formulated such that during use in aqueous operations, the wash water will have a pH of between 7 and 11, preferably between 8 and 10.5.

This invention further provides a method for cleaning dishware (i.e. glass, china, flatware and silverware) by contacting the dishware with a liquid detergent composition comprising detergent enzyme, detergent surfactant viscoelastic thixotropic thickening agent, enzyme stabilizing system, and buffering agent. Agitation is preferably provided for enhanced cleaning.

Preferred herein are concentrated gel and/or paste automatic dishwashing detergent compositions, more preferably gel automatic dishwashing detergent compositions. By "concentrated" or "compact" is meant that these compositions will deliver to the wash the same amount of active detergent ingredients at a lower dosage while achieving equal or improved performance. For example, in North America, dishwasher machines range in total dispenser cup capacity (many dishwashers have several dispenser cups) from 80 cc to 150 cc of product, depending on the machine manufacturer. Most current automatic dishwashing products are formulated to deliver the desired performance based on this dispensing volume. Compact products allow the reduction in the amount of product used to between 40% and 60%, but can range from 1% to 99%.

Process

Conventional methods can be used to prepare the viscoelastic, thixotropic liquid automatic dishwashing detergent compositions herein described. See, for example, U.S. Patents 4,824,590, Roselle, issued April 25, 1989, 5,053,158, Dixit et al, issued October 1, 1991, 4,970,016, Ahmed et al, issued November 13, 1990, 5,057,237, Drapier et al, issued October 15, 1991 and 5,078,027, Dixit et al, issued December 24, 1991. A preferred method for preparing a final product of the present invention comprises:

- (a) mixing water, enzyme stabilizers and pH adjusting agents under low to medium shear rate;
- (b) adding organic dispersant and builder;
- (c) adding under medium shearing a thickener slurry until a desired rheological property is achieved;
- (d) adding surfactant and other suitable agents; and
- (e) adding enzymes.

An alternate method is similar to the method herein above; however, the thickener is added after step (d) (adding surfactant and other suitable agents) and before the addition of enzymes. The thickener may be added as either a powder or slurry.

Whichever method is employed, the enzyme stabilizing system should be added prior to the addition of builder. Without being bound by theory, it is believed the enzyme stabilizing system added after the builder will associate with the builder and lose its effectiveness; whereas, if added prior to the builder it will form an effective compound which will not associate with the builder.

In addition, enzymes should be added last to minimize degradation due to temperature and pH changes resulting during the process.

All compositions prepared as above described exhibit a viscoelastic, thixotropic nature, and have good phase

stability.

The following examples illustrate the compositions of the present invention. All parts, percentages and ratios used herein are by stock weight unless otherwise specified.

5 EXAMPLE I

Concentrated gel automatic dishwashing detergent compositions of the present invention prepared according to the above described process are as follows:

Table 1

% by weight							
Ingredients	A	B	C	D	E	F	G
Potassium carbonate	2.00	4.00	0.00	9.73	3.50	0.00	0.25
Sodium carbonate	13.47	5.43	0.00	12.42	3.74	0.00	5.00
Sodium citrate dihydrate	0.00	15.00	25.00	0.00	0.00	0.00	0.00
Potassium hydroxide (45%)	0.00	0.00	4.98	0.00	8.44	17.78	0.67
Sodium hydroxide (50%)	0.00	0.00	0.00	0.00	3.00	7.72	0.00
Citric Acid (50%)	0.00	0.00	0.00	0.00	19.70	34.58	1.10
Monoethanolamine	1.91	1.91	1.91	1.91	1.91	1.91	1.91
Polyacrylate thickener (1)	2.00	2.00	2.00	1.75	2.00	2.00	2.00
Perfume	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Dye	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Sodium polyacrylate (45%) (2)	20.00	11.33	8.89	11.93	9.65	0.00	19.80
Polyoxypropylene-polyoxyethylene block copolymer (3)	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Boric Acid	2.00	2.00	2.00	2.00	2.00	2.00	2.00
1,2-propanediol (4)	4.50	4.50	4.50	4.50	4.50	4.50	4.50
Protease enzyme (5)	0.42	0.42	0.42	0.42	0.42	0.42	0.42
Amylase enzyme	0.42	0.42	0.42	0.42	0.42	0.42	0.42
Water and trim	-----balance-----						
pH	,10	,10	,10	,10	,10	,10	,10
K/Na ratio	0.20	0.25	0.33	1.04	0.83	0.92	0.07

(1) Polygel DK, 3V Chemical Corporation

(2) Acusol 445N or Acusol 480N, Rohm and Haas, Incorporated

(3) PluronicR 25R2, BASF Corporation

(4) SavinaseR 32.0 L EX, Novo Nordisk Industries, Incorporated

(5) MaxamylR WL 15,000, Gist-Brocades USA Incorporated

Table 2

% by weight					
Ingredients	H	I	J	K	L
Potassium carbonate	0.00	7.50	4.00	4.00	4.00
Sodium carbonate	0.00	7.50	5.43	5.43	5.43
Sodium citrate dihydrate	0.00	0.00	15.00	15.00	15.00
Potassium hydroxide (45%)	8.00	0.00	0.00	0.00	0.00

Table 2 (continued)

% by weight					
Ingredients	<u>H</u>	<u>I</u>	<u>J</u>	<u>K</u>	<u>L</u>
Sodium hydroxide (50%)	5.97	0.00	0.00	0.00	0.00
Citric Acid (50%)	38.57	0.00	0.00	0.00	0.00
Monoethanolamine	1.91	20.00	0.00	1.91	1.91
Aluminum tristearate	0.00	0.00	0.10	0.10	0.10
Polyacrylate thickener (1)	1.70	2.00	2.00	2.00	2.00
Perfume	0.05	0.05	0.10	0.10	0.10
Dye	0.000	0.000	0.002	0.002	0.002
Sodium polyacrylate (45%) (2)	8.89	10.00	11.30	11.30	11.30
Polyoxypropylene-polyoxyethylene block copolymer (3)	2.50	0.00	2.50	2.50	2.50
Suds suppressor (4)	0.00	0.00	0.00	1.00	0.00
Boric Acid	1.95	1.95	2.00	2.00	2.00
Sodium formate	0.00	0.00	0.00	0.00	0.20
Calcium formate	0.00	0.00	0.00	0.00	0.45
Sodium cumene sulfonate	1.35	0.00	0.00	0.00	0.00
1,2-propanediol (5)	4.50	4.50	4.50	4.50	4.50
Protease enzyme (6)	0.42	0.42	0.42	0.42	0.42
Amylase enzyme (7)	0.22	0.22	0.42	0.42	0.42
Lipase enzyme	0.00	0.00	0.00	0.30	0.30
Water and trim	-----balance-----				
pH Finished product	,8	,10	,10	,10	,10
K/Na ratio	0.54	1.33	.25	25	.25

(1) Polygel DK, 3V Chemical Corporation

(2) Acusol 445N or Acusol 480N, Rohm and Haas, Incorporated

(3) PluronicR 25R2, BASF Corporation

(4) LPKN, Knapsack

(5) SavinaseR 32.0 L EX, Novo Nordisk Industries, Incorporated

(6) MaxamylR WL 15,000, Gist-Brocades USA Incorporated

(7) Lipolase 100L Novo-Nordisk

Claims

1. A concentrated, viscoelastic, thixotropic, liquid automatic dishwashing detergent composition comprising, by weight:

(a) from 5% to 50% of a non-phosphate detergent builder selected from the group consisting of water-soluble, alkali metal, ammonium or substituted ammonium carbonates, bicarbonates, borates, polyhydroxysulfonates, polyacetates, carboxylates, polycarboxylates and mixtures thereof;

(b) from 0.0001 % to 5% of active detergent enzyme, preferably selected from the group consisting of protease, lipase, amylase and mixtures thereof;

(c) from 0.1% to 10% of viscoelastic, thixotropic thickener, preferably selected from the group consisting of cross-linked polycarboxylate polymers having a molecular weight of at least 500,000, natural gums, clays, cellulosic-type polymers and mixtures thereof;

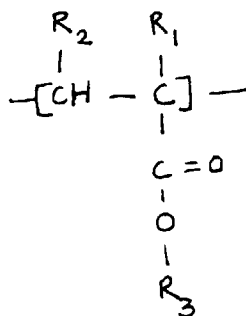
(d) sufficient pH adjusting agent to provide said composition with a product pH between 7 and 11; and

(e) from 0.001% to 20% of an enzyme stabilizing system selected from the group consisting of calcium ion,

propylene glycol, short chain carboxylic acid having a chain length of one carbon atom, polyhydroxyl compounds, boric acid, boronic acid, peptide aldehydes, and mixtures thereof; and
(f) water, wherein the aqueous phase includes both potassium and sodium ions at a K/Na weight ratio of at least 0.01, preferably between 0.01 and 10;

wherein said composition is substantially free of chlorine bleach, silicate, and phosphate.

2. The composition of Claim 1 further comprising from 0.1% to 20% of a detergent surfactant selected from the group consisting of capped propylene oxide, ethylene oxide block copolymers; condensation products of ethylene oxide and propylene oxide with a mono-, di-, or polyhydroxyl compound with residual hydroxyls capped; alkali metal salts of mono- and/or di-(C₈₋₁₄) alkyl diphenyl oxide mono- and/or di-sulfonates; C₈₋₁₈ alkyl sulfates; C₈₋₁₈ alkyl sulfonates; and mixtures thereof.
3. The composition according to Claim 1 or 2 comprising from 8% to 40% of said detergency builder and from 0.001 % to 1 % of said active deterative enzyme.
4. The composition according to any one of the preceding claims further comprising from 0.5% to 30% of an organic dispersant, preferably a low molecular weight water-soluble sodium polyacrylate of molecular weight from 1000 to 500,000, and from 0.01% to 6% of a chlorine scavenger, preferably monoethanol amine.
5. The composition according to any one of the preceding claims wherein said product pH is between 8 and 10.5 and wherein said pH adjusting agent is selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, sodium sesquicarbonate, sodium anhydrous sodium tetraborate, sodium tetraborate pentahydrate, potassium hydroxide, sodium hydroxide, a sodium tetraborate decahydrate, monoethanol amine, triethanol amine, and mixtures thereof.
6. The composition according to any one of the preceding claims further comprising from 0.1% to 15% of water-soluble peroxygen compounds.
7. The composition according to any one of the preceding claims comprising from 0.25% to 5% of said polycarboxylate polymer thickening agent and wherein said viscoelastic thixotropic thickener is a polycarboxylate polymer thickening agent with a molecular weight from 750,000 to 4,000,000.
8. The composition according to any one of the preceding claims wherein said detergency builder is the alkali metal of citrate or carbonate or mixtures thereof, preferably from 10% to 30% carbonate.
9. The composition according to any one of the preceding claims and comprising from 0.01% to 15% of said enzyme stabilizing system wherein said enzyme stabilizing system is selected from the group consisting of boric acid, 1,2-propanediol, calcium formate, sodium formate, peptide aldehyde and mixtures thereof.
10. The composition according to any one of the preceding claims wherein said active deterative enzyme is a protease or amylase or mixture thereof and said K/Na ratio is between 0.05 and 1.5.
11. The composition according to any of claims 4 to 10 wherein said polyacrylate copolymer of molecular weight from 1000 to 500,000 is a modified polyacrylate is defined as a copolymer which contains as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula:



wherein at least one of the substituents R_1 , R_2 or R_3 , preferably R_1 or R_2 is a 1 to 4 carbon alkyl or hydroxyalkyl group, R_1 or R_2 can be a hydrogen and R_3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_1 is methyl, R_2 is hydrogen and R_3 is sodium.

12. A concentrated gel automatic dishwashing detergent composition comprising, by weight:

- (a) from 5.0% to 40% of a non-phosphate detergency builder;
- (b) from 0.0001% to 5 % of an active deterative enzyme;
- (c) from 0.1% to 10% of a viscoelastic, thixotropic thickener;
- (d) from 0.001% to 10% of an enzyme stabilizing system selected from the group consisting of calcium ion, propylene glycol, short chain carboxylic acid having chain length of one carbon atom, boric acid, boronic acid and mixtures thereof;
- (e) from 0.1% to 30% of a detergent surfactant;
- (f) from 0.01% to 6% of a chloring scavenger;
- (g) sufficient buffering agent to provide said composition with a product pH between 7 and 11;
- (h) from 0.5% to 30% of low molecular weight polyacrylate polymer; and
- (i) water, wherein the aqueous phase includes both potassium and sodium ions at a K:Na weight ratio of from 0.01 to 10;

wherein said composition is substantially free of chlorine bleach, silicate, and phosphate.

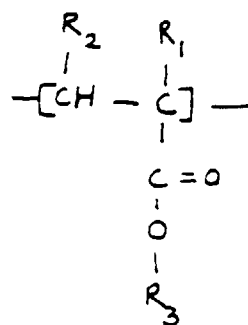
Patentansprüche

1. Konzentrierte, viskoelastische, thixotrope, flüssige Reinigerzusammensetzung zum maschinellen Geschirrspülen, umfassend, bezogen auf Gewicht:

- (a) 5 bis 50 % eines Nichtphosphat-Waschmittelbuilders, gewählt aus der wasserlösliche Alkalimetall-, Ammonium- oder substituierte Ammoniumcarbonate, Bicarbonate, Borate, Polyhydroxysulfonate, Polyacetate, Carboxylate, Polycarboxylate und Mischungen hiervon umfassenden Gruppe;
- (b) 0,0001 bis 5 % aktives Waschenzym, vorzugsweise gewählt aus der Protease, Lipase, Amylase und Mischungen hiervon umfassenden Gruppe;
- (c) 0,1 bis 10 % eines viskoelastischen, thixotropen Verdickungsmittels, vorzugsweise gewählt aus der vernetzte Polycarboxylatpolymere mit einem Molekulargewicht von mindestens 500.000, natürliche Gummen, Tone, Polymere vom Cellulose Typ und Mischungen hiervon umfassenden Gruppe;
- (d) ausreichend pH-Einstellungsmittel, um die Zusammensetzung mit einem Produkt-pH zwischen 7 und 11 zu versehen; und
- (e) 0,001 bis 20 % eines Enzymstabilisierungssystems, gewählt aus der Calciumionen, Propylenglykol, kurzkettige Carbonsäure mit einer Kettenlänge von einem Kohlenstoffatom, Polyhydroxylverbindungen, Borsäure, Boronsäure, Peptidalehyde und Mischungen hiervon umfassenden Gruppe; und
- (f) Wasser, wobei die wäßrige Phase sowohl Kalium als auch Natriumionen in einem K/Na-Gewichtsverhältnis von mindestens 0,01, vorzugsweise zwischen 0,01 und 10, beinhaltet;

wobei die Zusammensetzung im wesentlichen frei an Chlorbleichmittel, Silicat und Phosphat ist.

2. Zusammensetzung nach Anspruch 1, umfassend weiterhin 0,1 bis 20 % eines Waschtensids, gewählt aus der Gruppe, bestehend aus gekapptem Propylenoxid, Ethylenoxid-Blockcopolymeren; Kondensationsprodukten aus Ethylenoxid und Propylenoxid mit einer Mono-, Di- oder Polyhydroxylverbindung, wobei die restlichen Hydroxylgruppen gekappt sind; Alkalimetallsalzen von Mono- und/oder Di-(C₈₋₁₄)-alkyldiphenyloxidmono- und/oder -disulfonaten; C₈₋₁₈-Alkylsulfaten; C₈₋₁₈-Alkylsulfonaten; und Mischungen hiervon.
3. Zusammensetzung nach Anspruch 1 oder 2, umfassend 8 bis 40 % des Waschmittelbuilders und 0,001 bis 1 % des aktiven Waschenzyms.
4. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend weiterhin 0,5 bis 30 % eines organischen Dispergiermittels, vorzugsweise ein niedermolekulargewichtiges wasserlösliches Natriumpolyacrylat mit einem Molekulargewicht von 1.000 bis 500.000, und 0,01 bis 6 % eines Chlorfängers, vorzugsweise Monoethanolamin.
5. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei der Produkt-pH zwischen 8 und 10,5 liegt, und wobei das pH-Einstellungsmittel aus der Gruppe gewählt ist, bestehend aus Natriumcarbonat, Natriumbicarbonat, Kaliumcarbonat, Natriumsesquicarbonat, wasserfreies Natriumtetraborat, Natriumtetraborat-pentahydrat, Kaliumhydroxid, Natriumhydroxid, einem Natriumtetraboratdecahydrat, Monoethanolamin, Triethanolamin und Mischungen hiervon.
6. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend weiterhin 0,1 bis 15 % wasserlöslicher Persauerstoffverbindungen.
7. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend 0,25 bis 5 % des Polycarboxylatpolymer-Verdickungsmittels, und wobei das viskoelastische, thixotrope Verdickungsmittel ein Polycarboxylatpolymer-Verdickungsmittel mit einem Molekulargewicht von 750.000 bis 4.000.000 ist.
8. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei der Waschmittelbuilder das Alkalimetall von Citrat oder Carbonat oder Mischungen hiervon ist, vorzugsweise 10 bis 30 % Carbonat.
9. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, umfassend 0,01 bis 15 % des Enzymstabilisierungssystems, wobei das Enzymstabilisierungssystem aus der Gruppe gewählt ist, bestehend aus Borsäure, 1,2-Propandiol, Calciumformiat, Natriumformiat, Peptidaldehyd und Mischungen hiervon.
10. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, wobei das aktive Waschenzym eine Protease oder Amylase oder Mischung hiervon ist, und das K/Na-Verhältnis zwischen 0,05 und 1,5 liegt.
11. Zusammensetzung nach mindestens einem der Ansprüche 4-10, wobei das Polyacrylatcopolymer mit einem Molekulargewicht von 1.000 bis 500.000 ein modifiziertes Polyacrylat ist, das definiert ist als ein Copolymer, welches als Monomereinheiten a) 90 bis 10 Gew.-%, vorzugsweise 80 bis 20 Gew.-%, Acrylsäure oder deren Salze, und b) 10 bis 90 Gew.-%, vorzugsweise 20 bis 80 Gew.-% eines substituierten Acrylmonomeren oder dessen Salze der allgemeinen Formel:



enthält, worin mindestens einer der Substituenten R₁, R₂ oder R₃, vorzugsweise R₁ oder R₂ eine Alkyl- oder Hydroxyalkylgruppe mit 1 bis 4 Kohlenstoffatomen ist, R₁ oder R₂ ein Wasserstoffatom sein kann, und R₃ ein Was-

serstoffatom oder Alkalimetallsalz sein kann; wobei am meisten bevorzugt ein substituiertes Acrylmonomer ist, worin R₁ Methyl ist, R₂ Wasserstoff ist und R₃ Natrium ist.

- 5 12. Konzentrierte, gelförmige Reinigerzusammensetzung zum maschinellen Geschirrspülen, umfassend, bezogen auf Gewicht:

- (a) 5,0 bis 40 % eines Nichtphosphat-Waschmittelbuilders;
 (b) 0,0001 bis 5 % eines aktiven Waschenzyms;
 (c) 0,1 bis 10 % eines viskoelastischen, thixotropen Verdickungsmittels;
 10 (d) 0,001 bis 10 % eines Enzymstabilisierungssystems, gewählt aus der Gruppe, bestehend aus Calciumionen, Propylenglykol, kurzkettiger Carbonsäure mit einer Kettenlänge von einem Kohlenstoffatom, Borsäure, Borsäure und Mischungen hiervon;
 (e) 0,1 bis 30 % eines Waschtensids;
 (f) 0,01 bis 6 % eines Chlorfängers;
 15 (g) ausreichend Puffermittel, um die Zusammensetzung mit einem Produkt-pH zwischen 7 und 11 zu versehen;
 (h) 0,5 bis 30 % eines niedermolekulargewichtigen Polyacrylatpolymeren; und
 (i) Wasser, wobei die wäßrige Phase sowohl Kalium- und Natriumionen bei einem K:Na-Gewichtsverhältnis von 0,01 bis 10 beinhaltet;

20 wobei die Zusammensetzung im wesentlichen frei ist an Chlorbleichmittel, Silicat und Phosphat.

Revendications

- 25 1. Composition détergente liquide concentrée, thixotrope, viscoélastique, pour le lavage automatique de la vaisselle, comprenant, en poids:

- (a) de 5% à 50% d'un adjuvant détergent non phosphate choisi dans le groupe constitué par les carbonates, les bicarbonates, les borates, les polyhydroxysulfonates, les polyacétates, les carboxylates, les polycarboxylates de métaux alcalins, d'ammonium ou d'ammonium substitué, solubles dans l'eau, et leurs mélanges;
 30 (b) de 0,0001% à 5% d'enzyme détersive active, de préférence choisie dans le groupe constitué par les enzymes protéase, lipase, amylase, et leurs mélanges;
 (c) de 0,1% à 10% d'un épaississant thixotrope, viscoélastique, de préférence choisi dans le groupe constitué par les polymères polycarboxylates réticulés ayant une masse moléculaire d'au moins 500 000, les gommes naturelles, les argiles, les polymères de type cellulosique et leurs mélanges;
 35 (d) suffisamment d'agent d'ajustement du pH pour procurer à ladite composition un pH de produit compris entre 7 et 11; et
 (e) de 0,001% à 20% d'un système stabilisateur d'enzyme choisi dans le groupe constitué par les ions calcium, le propylèneglycol, un acide carboxylique à chaîne courte avant une longueur de chaîne d'un atome de carbone, les composés polyhydroxylés, l'acide borique, un acide boronique, les aldéhydes peptidiques, et leurs mélanges; et
 40 (f) de l'eau, la phase aqueuse comprenant à la fois des ions potassium et des ions sodium dans un rapport pondéral de K/Na d'au moins 0,01, de préférence, compris entre 0,01 et 10;

45 ladite composition étant essentiellement dépourvue d'agent de blanchiment au chlore, de silicate et de phosphate.

2. Composition selon la revendication 1, comprenant en outre de 0,1% à 20% d'un tensioactif détergent choisi dans le groupe constitué par les copolymères séquencés bloqués d'oxyde de propylène et d'oxyde d'éthylène; les produits de condensation d'oxyde d'éthylène et d'oxyde de propylène avec un composé mono-, di- ou polyhydroxylé ayant des groupes hydroxyles résiduels bloqués; les sels de métaux alcalins de mono- et/ou de di-alkyl(en C₈₋₁₄) diphényloxyde mono- et/ou di-sulfonates; les alkyl(en C₈₋₁₈)sulfates; les alkyl(en C₈₋₁₈)sulfonates et leurs mélanges.
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3. Composition selon la revendication 1 ou 2, comprenant de 8% à 40% dudit adjuvant de détergence et de 0,001% à 1% de ladite enzyme détersive active.
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4. Composition selon l'une quelconque des revendications précédentes, comprenant en outre de 0,5% à 30% d'un dispersant organique, de préférence, un polyacrylate de sodium soluble dans l'eau, de faible masse moléculaire,

ayant une masse moléculaire de 1000 à 500 000, et de 0,01% à 6% d'un piègeur de chlore, de préférence, la monoéthanolamine.

5. Composition selon l'une quelconque des revendications précédentes, dans laquelle ledit pH de produit est compris entre 8 et 10,5, et dans laquelle ledit agent d'ajustement du pH est choisi dans le groupe constitué par le carbonate de sodium, le bicarbonate de sodium, le carbonate de potassium, le sesquicarbonate de sodium, le tétraborate de sodium anhydre, le tétraborate de sodium pentahydraté, l'hydroxyde de potassium, l'hydroxyde de sodium, un tétraborate de sodium décahydraté, la monoéthanolamine, la triéthanolamine, et leurs mélanges.

6. Composition selon l'une quelconque des revendications précédentes, comprenant en outre de 0,1% à 15% de composés peroxygénés solubles dans l'eau.

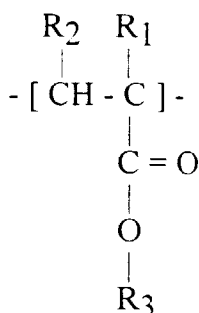
7. Composition selon l'une quelconque des revendications précédentes, comprenant de 0,25% à 5% dudit agent épaississant polymère polycarboxylate et dans laquelle ledit épaississant thixotrope, viscoélastique est un agent épaississant polymère polycarboxylate ayant une masse moléculaire de 750 000 à 4 000 000.

8. Composition selon l'une quelconque des revendications précédentes, dans laquelle ledit adjuvant de détergence est un citrate ou un carbonate de métal alcalin ou leurs mélanges, de préférence de 10% à 30% de carbonate.

9. Composition selon l'une quelconque des revendications précédentes, comprenant de 0,01% à 15% dudit système stabilisateur d'enzyme, ledit système stabilisateur d'enzyme étant choisi dans le groupe constitué par l'acide borique, le 1,2-propanediol, le formiate de calcium, le formiate de sodium, un aldéhyde peptidique et leurs mélanges.

10. Composition selon l'une quelconque des revendications précédentes, dans laquelle ladite enzyme détersive active est une protéase ou une amylase, ou leur mélange, et ledit rapport K/Na est compris entre 0,05 et 1,5.

11. Composition selon l'une quelconque des revendications 4 à 10, dans laquelle ledit copolymère de polyacrylate ayant une masse moléculaire de 1000 à 500 000 est un polyacrylate modifié qui est défini comme étant un copolymère contenant comme motifs monomères: a) de 90% à 10%, de préférence de 80% à 20%, en poids d'acide acrylique ou de ses sels et b) de 10% à 90%, de préférence de 20% à 80%, en poids d'un monomère acrylique substitué ou de ses sels, de formule générale:



dans laquelle au moins l'un des substituants R_1 , R_2 ou R_3 , de préférence R_1 ou R_2 , est un groupe alkyle ou hydroxyalkyle de 1 à 4 atomes de carbone, R_1 ou R_2 peut être un atome d'hydrogène et R_3 peut être un atome d'hydrogène ou un sel de métal alcalin; un monomère acrylique substitué étant particulièrement préféré, où R_1 est un groupe méthyle, R_2 est un atome d'hydrogène et R_3 est un sodium.

12. Composition détergente en gel concentrée pour le lavage automatique de la vaisselle, comprenant, en poids;

(a) de 5,0% à 40% d'un adjuvant de détergence non phosphate;

(b) de 0,0001% à 5% d'une enzyme détersive active;

(c) de 0,1% à 10% d'un épaississant thixotrope, viscoélastique;

(d) de 0,001% à 10% d'un système stabilisateur d'enzyme choisi dans le groupe constitué par les ions calcium, le propylène glycol, un acide carboxylique à chaîne courte ayant une longueur de chaîne d'un atome de carbone, l'acide borique, un acide boronique, et leurs mélanges;

(e) de 0,1% à 30% d'un tensioactif détergent;

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(f) de 0,01% à 6% d'un piègeur de chlore;

(g) suffisamment d'un agent tampon pour procurer à ladite composition un pH de produit compris entre 7 et 11;

(h) de 0,5% à 30% de polymère polyacrylate de faible masse moléculaire; et

(i) de l'eau, la phase aqueuse comprenant à la fois des ions potassium et des ions sodium dans un rapport pondéral de K/Na de 0,01 à 10;

ladite composition étant essentiellement dépourvue d'agent de blanchiment au chlore, de silicate et de phosphate.