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GB 1529713 A GB 1473571 A

(58) Field of search

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(54) **Thickened aqueous no- or low- phosphate built cleaning composition**

(57) A no- or low- (less than 0.01%) phosphorus built aqueous liquid (e.g. automatic dishwasher) detergent composition is based on a mixture of aluminosilicate zeolite and a bleach-stable, water-soluble, carboxyl group-containing polymer, such as sodium polyacrylate, to achieve comparable cleaning performance to a phosphate built formulation. The preferred compositions which include inorganic colloid forming clay and aliphatic fatty acid or salt thereof, are viscoelastic and physically stable against phase separation. The compositions contain alkali metal silicate and a chlorine bleach.

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THICKENED AQUEOUS NO- OR LOW-
PHOSPHATE BUILT CLEANING COMPOSITION

5 The present invention relates to aqueous cleaning compositions for cleaning dishes and the like, especially in an automatic dishwasher. More specifically, the invention relates to such compositions which do not include any phosphate builders but which give comparable or superior cleaning performance to similar phosphorus containing liquid automatic dishwasher detergent compositions.

10 The present invention specifically relates to thickened liquid automatic dishwashing detergent compositions having viscoelastic properties, improved chemical and physical stability, and with increased cleaning performance despite the absence of phosphate builder salts and which are readily dispersible in the washing medium to provide effective cleaning of dishware, glassware, china and the like.

15 Commercially available household-machine dishwasher detergents provided in power form have several disadvantages, e.g. non-uniform composition; costly operations necessary in their manufacture; tendency to cake in storage at high humidities, resulting in the formation of lumps which are difficult to disperse; dustiness, a source of particular irritation to users who suffer allergies; and tendency to cake in the dishwasher machine dispenser. Liquid forms of such compositions, however, generally cannot be used in automatic dishwashers due to high foam levels, unacceptably low viscosities and exceedingly high alkalinity.

20 Recent research and development activity has

focused on the gel or "thixotropic" form of such compositions, e.g. scouring cleansers and automatic-dishwasher products characterized as thixotropic liquids or pastes. Dishwasher products so provided are primarily objectionable in that they are insufficiently viscous to remain "anchored" in the dispenser cup of the dishwasher, and moreover yield spotty residues on dishware, glassware, china and the like.

The provision of automatic-dishwasher compositions in gel form having satisfactory dispensing stability and cleaning properties has thus far proven problematical, particularly as regards compositions for use in home dishwasher machines. For effective use, it is generally recommended that the automatic dishwashing detergent, hereinafter also designated ADD, contain (1) sodium tripolyphosphate (NaTPP) to soften or tie up hardwater materials and to emulsify and/or peptize soil; (2) sodium silicate to supply the alkalinity necessary for effective detergency and to provide protection for fine china glaze and pattern; (3) sodium carbonate, generally considered to be optional, to enhance alkalinity; (4) a chloride-releasing agent to aid in the elimination of soil specks which lead to water spotting; and (5) defoamer/surfactant to reduce foam, thereby enhancing machine efficiency and supplying requisite detergency. See, for example, SDA Detergents in Depth, "Formulations Aspects of Machine Dishwashing," Thomas Oberle (1974). Cleaners approximately to the aforescribed compositions are mostly liquids or powders. Combining such ingredients in the thickened form effective for home-machine use has proved difficult. Generally, such compositions omit

hypochlorite bleach, since it tends to react with other chemically active ingredients, particularly surfactant, thereby degrading the suspending or thickening agent and impairing its effectiveness.

5 U.S. Patent 4,115,308 discloses thixotropic automatic dishwasher pastes containing a suspending agent, e.g. CMC, synthetic clays or the like; inorganic salts including silicates, phosphates and polyphosphates; a small amount of surfactant and a suds
10 depressor. Bleach is not disclosed. On the other hand, U.S. Patent 3,684,722 discloses alkali metal hypochlorite bleaching and cleaning composition thickened with mixtures of C₈-C₁₈ alkali metal soaps and hydrotropes, such as amine oxide and betaines. The
15 patentees describe tests that show that various classes of organic polymer thickeners were either unstable or otherwise failed to provide adequate thickening or resulted in loss of available chlorine. The polyacrylates were found to provide thickening for
20 several weeks at room temperature but then decomposed.

U.S. Patent 3,985,668 describes abrasive scouring cleaners of gel-like consistency containing (1) suspending agent, preferably the Smectite and attapulgite types of clay; (2) abrasive, e.g. silica
25 sand or perlite; and (3) filler comprising light density powdered polymers, expanded perlite and the like, which has a buoyancy and thus stabilizing effect on the composition in addition to serving as a bulking agent, thereby replacing water otherwise available for
30 undesired supernatant layer formation due to leaking and phase destabilization. The foregoing are the essential ingredients. Optional ingredients include hypochlorite bleach, bleach stable surfactant and

buffer, e.g. silicates, carbonates, and monophosphates. Builders, such as NaTPP, can be included as further optional ingredients to supply or supplement building functions not provided by the buffer, the amount of such builder not exceeding 5% of the total composition, according to the patent. Maintenance of the desired (greater than) pH 10 levels is achieved by the buffer/builder components. High pH is said to minimize decomposition of chlorine bleach and undesired interaction between surfactant and bleach. When present, NaTPP is limited to 5%, as stated. Foam killer is not disclosed.

In U.K. Patent Applications GB 2,116,199A and GB 2,140,450A, both of which are assigned to Colgate-Palmolive, liquid ADD (LADD) compositions are disclosed which have properties desirably characterizing thixotropic, gel-type structure and which have various ingredients necessary for effective detergency with an automatic dishwasher detergent composition having thixotropic properties includes the following ingredients, on a weight basis:

- (a) 5 to 35% alkali metal tripolyphosphate;
- (b) 2.5 to 20% sodium silicate;
- (c) 0 to 9% alkali metal carbonate;
- (d) 0.1 to 5% chlorine bleach stable, water dispersible organic detergent active material;
- (e) 0 to 5% chlorine bleach stable foam depressant;
- (f) chlorine bleach compound in an amount to provide about 0.2 to 4% of available chlorine;
- (g) thixotropic thickener in an amount sufficient to provide the composition with a thixotropy index of about 2.5 to 10;

(h) sodium hydroxide, as necessary, to adjust pH; and

(i) water.

LADD compositions so formulated are low-foaming; are readily soluble in the washing medium and most effective at alkaline pH values. The compositions are normally of gel consistency, i.e. a highly viscous, opaque jelly-like material having Bingham plastic character and thus relatively high yield values. Accordingly, a definite shear force is necessary to initiate or increase flow, such as would obtain within the agitated dispenser cup of an energized automatic dishwasher. Under such conditions, the composition is quickly fluidized and easily dispersed. When the shear force is discontinued, the fluid composition quickly reverts to a high viscosity, Bingham plastic state closely approximating its prior consistency.

U.S. Patent 4,511,487, dated April 16, 1985, describes a low-foaming detergent paste for dishwashers. The patented thixotropic cleaning agent has a viscosity of at least 30 pa.s at 20°C as determined with a rotational viscometer at a spindle speed of 5 revolutions per minute. The composition is based on a mixture of finely divided hydrated sodium tripolyphosphate and thickening agent which is a foliated silicate of the hectorite type. Small amounts of nonionic tensides and alkali metal carbonates and/or hydroxides may be used.

Recently, applicant has developed various modifications and improvements in liquid automatic dishwasher detergent compositions of GB 2,116,199A and GB 2,140,450A. For example U.S. Application Serial No. 816,835 corresponding to GB Application No. 8700139

Serial No. 2185037 discloses aqueous gel-like thixotropic clay-free and polymer thickener-free liquid cleaning compositions which utilize a mono- or polycarboxylic acid having from 8 to 22 carbon atoms to impart physical stability and thixotropic properties.

In commonly assigned copending application U.S. Serial No. 903,924 corresponding to GB Application No. 8720698 Serial No. 2194954 the physical stability of clay based thixotropic liquid built automatic dishwashing detergency compositions is improved by addition thereto of small amounts, for example, from about 0.02 to 1% by weight, of a polyvalent metal salt of a long chain fatty acid, such as aluminium stearate.

The majority of these disclosed and commercial liquid automatic dishwasher detergent and similar compositions depend upon phosphate builder salts, such as sodium tripolyphosphate, to enhance cleaning performance. While the phosphate builder salts are highly effective for this purpose, their use has a major disadvantage: they are harmful to aquatic life and to the waterways, in general. In fact, many jurisdictions have or are considering a general ban on phosphate containing cleaning detergent products.

Although there have been many attempts to provide alternative builders and many such non-phosphate inorganic and organic detergent builder salts are known very few are capable in practice of providing comparable cleaning benefits to the phosphate builders. Furthermore, selection of suitable builders is even more difficult in the environment of the present bleach containing aqueous compositions since the alternative builder must be chlorine bleach compatible.

In addition to its function as a detergency

builder, the inorganic alkali metal phosphate salt builder provides an important function in contributing to the rheological properties of the thickened thixotropic gel-like liquid aqueous detergent compositions such as described above in GB 2,116,199A and GB 2,140,450A. Accordingly, replacing the phosphate builder with a non-phosphate builder has not proven to be a simple task since so many different factors must be taken into consideration in fulfilling all of the multifunctional tasks of the phosphate builder.

The invention aims to provide aqueous bleach containing cleaning compositions which avoid the use of phosphate builders and contain no or only environmentally tolerable levels of phosphorus from other sources.

The invention also aims to provide no or low phosphate thickened liquid ADD compositions with improved physical stability and rheological properties.

The invention also aims to provide thickened liquid ADD compositions having no or low levels of phosphorus without adversely affecting or while improving cleaning performance, particularly low spot and film formation.

According to the present invention there is provided an aqueous liquid low- or no-phosphorus cleaning composition comprising water, chlorine bleach-stable water dispersible organic detergent, chlorine bleach, alkali metal silicate and detergent builder, wherein the detergent builder comprises a mixture of aluminosilicate zeolite and carboxyl group-containing bleach-stable water-soluble polymer, or a salt thereof. More particularly, according to a preferred and

specific embodiment of the invention, there is provided a thickened viscoelastic liquid automatic dishwasher detergent composition which is free of phosphate builder salts and contains no or only low levels of phosphorus and which is effective to inhibit settling of the water-insoluble suspended particles, such as the aluminosilicate zeolite builder, bleach particles, etc. The composition may include clay or other thickeners as well as other stabilizing agents and other conventional ADD additives.

In accordance with this particular aspect, the present invention provides a normally gel-like aqueous automatic dishwasher detergent composition having viscoelastic properties which include, on a weight basis:

- (a) 5 to 35% aluminosilicate zeolite;
- (b) 25 to 40% sodium silicate;
- (c) 0 to 9% alkali metal carbonate;
- (d) 0.1 to 5% chlorine bleach stable, water dispersible organic detergent active material;
- (e) 0 to 5% chlorine bleach stable foam depressant;
- (f) chlorine bleach compound in an amount to provide about 0.2 to 4% of available chlorine;
- (g) 0 to 0.5% of a long chain fatty acid or salt thereof;
- (h) 0 to 5% of a clay thickener;
- (i) 0 to 8% sodium hydroxide; and
- (j) balance water.

Also related to this specific aspect, the invention provides a method for cleaning dishware in an automatic dishwashing machine with an aqueous wash bath containing an effective amount of the liquid automatic

dishwasher detergent (LADD) composition as described above. According to this aspect of the invention, the LADD composition can be readily poured into the dispensing cup of the automatic dishwashing machine and
5 will be sufficiently viscous, to remain securely within the dispensing cup until shear forces are applied thereto, such as by the water spray from the dishwashing machine, whereupon the yield value of the composition will be exceeded and the composition will
10 flow.

In view of environmental concerns stemming from the problem of eutrication of lakes, rivers and other waterways attributed to the deposition of phosphorus from detergents and other products into the waterways,
15 there has been a good deal of emphasis on removing phosphates from detergent products.

However, attempts to replace the phosphate builder from thixotropic liquid automatic dishwasher compositions of the type used by the assignee of the
20 subject application and which typically include 0 to 3% clay thickener - generally of the smectite water - swelling type; 10 to 25% of alkali metal silicate; 0 to 0.5% fatty acid stabilizer; small amounts of bleach, bleach stable detergent, bleach stable anti-foam agent,
25 sodium carbonate, caustic soda and the like, and about 20 to 25% of alkali metal phosphate salt as detergent builder, have resulted in loss of thixotropic properties and usually worsening of cleaning performance. Although the exact mechanism of the
30 disruption of the rheological properties causing loss of thixotropy has not been fully elucidated it appears that there is at least some interaction between the suspended phosphate builder particles and the other

ingredients of the formulation, especially the clay thickener and fatty acid or fatty acid salt stabilizer and this interaction contributes to increasing the yield stress and plastic viscosity of the composition.

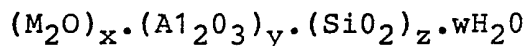
5 The present invention is based upon the surprising discovery that similar rheological properties and physical stability, i.e. resistance to phase separation, settling, etc., as in these prior phosphate-built liquid aqueous ADD compositions can be
10 achieved by including in the composition aluminosilicate zeolite as an inorganic water-insoluble detergent builder in mixture with bleach stable, water-soluble, carboxyl group containing polymer as a multifunctional rheological agent and detergent builder
15 and by increasing the level of the alkali metal silicate to more than 25% by weight. At the same time, improvements in spotting and filming performance (i.e. fewer spots and reduced filming) can be achieved.

 Although the compositions of the present invention
20 do not exhibit thixotropic properties, they do exhibit viscoelastic properties and have a yield point (the maximum stress in a curve of shear stress versus shear rate) sufficiently high that they will not flow under the force exerted by their own weight, i.e.
25 gravitational forces. Therefore the compositions of the present invention can be easily poured into the dispenser cup of an automatic dishwashing machine and will not flow out until a sufficiently high shear stress, such as the force of the water jets impinging
30 on the cup during the detergent dispersing cycle, is applied.

 Of course, it is understood that where physical stability for extended periods of several weeks or

months is not required and where it is not required to provide a highly thickened solution, the high levels of silicate, the clay thickener and/or fatty acid or fatty acid salt stabilizer can be omitted from the formulation without adversely effecting the cleaning performance provided by the aluminosilicate zeolite builder and the water-soluble carboxyl group- (or salt thereof) containing bleach stable polymer.

The builders useful herein are the water-insoluble aluminosilicates, both of the crystalline and amorphous type. Various crystalline zeolites are described in British Patent 1,504,168, U.S. Patent 4,409,136 and Canadian Patents 1,072,835 and 1,087,477, all of which are hereby incorporated by reference for such descriptions. An example of amorphous zeolites useful herein can be found in Belgium Patent 835,351 and this patent, too, is incorporated herein by reference. The zeolites generally have the formula

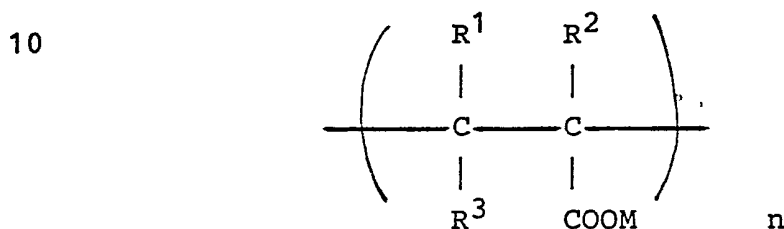


wherein x is 1, y is from 0.8 to 1.2 and preferably 1, z is from 1.5 to 3.5 or higher and preferably 2 to 3 and w is from 0 to 9, preferably 2.5 to 6 and M is an alkali metal, preferably sodium or potassium, especially preferably sodium. A typical zeolite is type A or similar structure, with type 4A particularly preferred. The preferred aluminosilicates have calcium ion exchange capacities of about 200 milliequivalents per gram or greater, e.g. 400 meq/g.

The aluminosilicate zeolite builder can be present in the formulations in the same quantities as found useful for the alkali metal polyphosphate builders, generally in the range of from about 5 to 35 weight percent, preferably about 20 to 30 weight percent.

The carboxyl group-containing bleach-stable water-soluble polymers useful herein include, for example, the acrylic acid homopolymers and copolymers and their salts. These materials are generally commercially available and can be described as follows.

The polyacrylic acid polymers and their salts that can be used comprise water-soluble low molecular weight polymers having the formula



wherein the R^1 , R^2 and R^3 can be the same or different and each represent a hydrogen atom or a C_1 - C_4 lower alkyl group, or combinations thereof; n is a number from 5 to 250, preferably 10 to 150, and more preferably 20 to 100; and M represents hydrogen, or an alkali metal, such as sodium or potassium. The preferred substituent for M is sodium.

The preferred R^1 , R^2 and R^3 groups are hydrogen, methyl, ethyl and propyl. The preferred acrylic monomer is one where R^1 and R^3 are hydrogen, e.g. acrylic acid, or where R^1 and R^3 are hydrogen and R^2 is methyl, e.g. methacrylic acid monomer.

The degree of polymerization, i.e. the value of n , is generally determined by the limit compatible with the solubility of the polymer or copolymer in water. The terminal or end groups of the polymer or copolymer are not critical and can be H, OH, CH_3 or a low molecular weight hydrocarbon.

Typically the polyacrylic acid copolymers can include copolymers of, for example, acrylic acid or methacrylic acid and a polycarboxylic acid anhydride or acid, such as succinic anhydride, succinic acid, maleic acid, maleic anhydride, citric acid and the like. Copolymers of acrylic or methacrylic acid with maleic anhydride are preferred.

The acrylic acid or methacrylic acid monomer will usually comprise 40-60 weight percent, e.g. about 50 weight percent of the copolymer with a polycarboxylic acid or anhydride.

The polyacrylic acid polymer can have a molecular weight (weight average) of 500 or 1,000 to 25,000, preferably 1,500 to 15,000 and especially preferably 2,000 to 10,000. The copolymers can have higher molecular weights, for example, up to about 100,000.

Specific examples of polyacrylic acid polymers which can be used include the Acrysol LMW acrylic acid polymers from Rohm and Haas, such as the Acrysol LMW-45NX, a neutralized sodium salt, which has a molecular weight of about 4,500 and Acrysol LMW-20NX, a neutralized sodium salt, which has a molecular weight of about 2,000.

A specific example of a polyacrylic acid copolymer that can be used is Sokalan CP5 (from BASF) which has a molecular weight of about 70,000 and is the reaction product of about equal moles of methacrylic acid and maleic anhydride which has been completely neutralized to form the sodium salt thereof.

The above polymers and copolymers can be made using procedures known in the art. See, for example, U.S. Patent 4,203,858.

The water-soluble carboxyl group-containing

bleach-stable polymers have been found to provide three primary functions in the liquid automatic dishwasher detergent compositions of this invention: rheology control; calcium sequestering; and soil dispersing.

5 As a rheology control agent, the polymer additive apparently functions as a thickener and together with the high levels of alkali metal silicate, clay (when present) and fatty acid or salt (when present), to impart viscoelasticity to the composition and a plastic
10 viscosity in the range of from about 200 to 10,000 centipoise, preferably 2,000 to 8,000 cps, such as 5,000 cps. The desired viscoelasticity and plastic viscosity ranges are best achieved when the molecular weight is no more than 10,000, especially from 2,000 to
15 10,000, such as about 4,000 to 5,000.

As a calcium sequestering agent it is important that the polymer have especially good water solubility. Here again, best results are achieved when the polymer has a molecular weight of 10,000 or less, especially
20 2,000 to 10,000.

Similarly as a soil dispersing agent contributing to the desired improved anti-spotting and anti-filming properties, molecular weights of the polymer additive are preferably in the range of 2,000 to 10,000.

25 The amount of the polyacrylic acid polymer or copolymer additive needed to achieve the desired enhancement of physical stability and cleaning performance will depend on such factors as the amount and nature of the fatty acid or salt (when present),
30 the nature and amount of the clay thickener (when present), detergent active compound, bleaching agent, as well as the anticipated storage and shipping conditions.

Generally, however, amounts of the polyacrylic acid polymer or copolymer additive that can be used are in the range of from about 0.5 to 10% by weight, preferably from about 0.80 to 8.0 weight percent, especially preferably about 2 to 6 weight percent.

Detergent active material useful herein must be stable in the presence of chlorine bleach, especially hypochlorite bleach, and those of the organic anionic, amine oxide, phosphine oxide, sulphoxide or betaine water dispersible surfactant types are preferred, the first mentioned anionics being most preferred. They are used in amounts ranging from about 0.1 to 5%, preferably about 0.3 to 2.0%. Particularly preferred surfactants herein are the linear or branched alkali metal mono- and/or di-(C₈-C₁₄) alkyl diphenyl oxide mono and/or disulphates, commercially available for example as DOWFAX (registered trademark) 3B-2 and DOWFAX 2A-1. In general, the paraffin sulphonates tend to unduly increase viscosity causing severe shearing force problems. In addition, the surfactant should be compatible with the other ingredients of the composition. Other suitable surfactants include the primary alkylsulphates, alkylsulphonates, alkylarylsulphonates and sec.-alkylsulphates. Examples include sodium C₁₀-C₁₈ alkylsulphates, such as sodium dodecylsulphate and sodium tallow alcoholsulphate; sodium C₁₀-C₁₈ alkanesulphonates, such as sodium hexadecyl-1-sulphonate and sodium C₁₁-C₁₈ alkylbenzenesulphonates, such as sodium dodecylbenzenesulphonates. The corresponding potassium salts may also be employed.

As other suitable surfactants or detergents, the amine oxide surfactants are typically of the structure

R_2R^1NO , in which R represents a lower alkyl group, for instance, methyl, and R^1 represents a long chain alkyl group having from 8 to 22 carbon atoms, for instance, a lauryl, myristyl, palmityl or cetyl group. Instead of an amine oxide, a corresponding surfactant phosphine oxide R_2R^1PO or sulfoxide RR^1SO can be employed. Betaine surfactants are typically of the structure $R_2R^1N - R''COO^-$, in which each R represents a lower alkylene group having from 1 to 5 carbon atoms. Specific examples of these surfactants are lauryldimethylamine oxide, myristyldimethylamine oxide, the corresponding phosphite oxides and sulfoxides, and the corresponding betaines, including dodecyldimethylammonium acetate, tetradecyldiethylammonium pentanoate, hexadecyldimethylammonium hexanoate and the like. For biodegradability, the alkyl groups in these surfactants should be linear, and such compounds are preferred.

Surfactants of the foregoing type, all well known in the art, are described, for example, in U.S. Patents 3,985,668 and 4,271,030.

Although any chlorine bleach compound may be employed in the compositions of this invention, such as dichloroisocyanurate, dichloro-dimethyl hydantoin, or chlorinated TSP, alkali metal, e.g. potassium, lithium, magnesium and especially sodium, hypochlorite is preferred. The composition should contain sufficient chlorine bleach compound to provide about 0.2 to 4.0% by weight of available chlorine, as determined, for example, by acidification of 100 parts of the composition with excess hydrochloric acid. A solution containing about 0.2 to 4.0% by weight of sodium hypochlorite contains or provides roughly the same

percentage of available chlorine. About 0.8 to 1.6% by weight of available chlorine is especially preferred. For example, sodium hypochlorite (NaOCl) solution of from about 11 to about 13% available chlorine in amounts of about 3 to 20%, preferably about 7 to 12%, can be advantageously used.

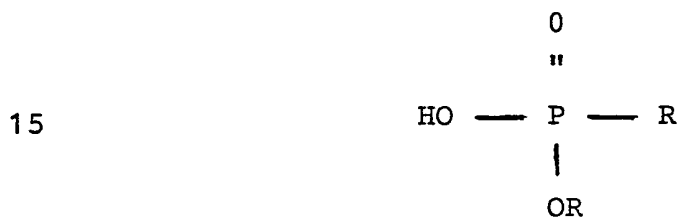
The sodium or potassium silicate, which provides alkalinity and protection of hard surfaces, such as fine china glaze and pattern, is normally employed in an amount ranging from about 2.5 to 20 or 25 weight percent. At levels greater than about 10 weight percent the silicate also provides increased anti-spotting action.

However, for the preferred viscoelastic, physically stable liquid aqueous dishwasher detergent compositions of this invention it is essential to incorporate quantities of the alkali metal silicate in excess of the amounts normally employed, especially more than 25 weight percent, for example, from 28% to 40%, especially from about 30 to 38%, by weight, of the composition.

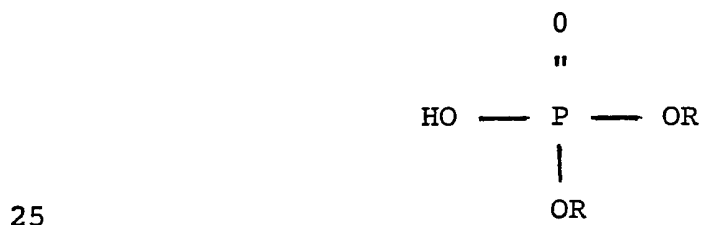
The sodium silicate is generally added in the form of an aqueous solution, preferably having an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.2 to 1:2.8, for example, 1:2.4. Most of the other components of the composition, especially NaOH, sodium hypochlorite and foam depressant may also be added in the form of an aqueous dispersion or solution.

Foam inhibition is important to increase dishwasher machine efficiency and minimize destabilizing effects which might occur due to the presence of excess foam within the washer during use. Foam may be sufficiently reduced by suitable selection

of the type and/or amount of detergent active material,
 the main foam-producing component. The degree of foam
 is also somewhat dependent on the hardness of the wash
 water in the machine whereby suitable adjustment of the
 5 proportions of NaTPP which has a water softening effect
 may aid in providing the desired degree of foam
 inhibition. However, it is generally preferred to
 include a chlorine bleach stable foam depressant or
 inhibitor. Particularly effective in this regard,
 10 where some phosphorus content can be tolerated, are the
 alkyl phosphonic acid esters of the formula



and especially the alkyl acid phosphate esters of the
 20 formula



In the above formulas, one or both R groups in each
 type of ester may represent independently a C₁₂-C₂₀
 alkyl group. The ethoxylated derivatives of each type
 30 of ester, for example, the condensation products of one
 mole of ester with from 1 to 10 moles, preferably 2 to
 6 moles, more preferably 3 or 4 moles, ethylene oxide
 can also be used. Some examples of the foregoing are

commercially available, such as the products SAP from Hooker and LPKn-158 from Knapsack. Mixtures of the two types, or any other chlorine bleach stable types, or mixtures of mono- and diesters of the same type, may be employed. Especially preferred is a mixture of mono- and di-C₁₆-C₁₈ alkyl acid phosphate esters such as monostearyl/distearyl acid phosphates 1.2/1, and the 3 to 4 mole ethylene oxide condensates thereof. When employed, proportions of 0.01 to 0.5 weight percent, preferably 0.02 to 0.4 weight percent, especially about 0.1 to 0.2 weight percent, of foam depressant in the composition is typical, the weight ratio of detergent active component to foam depressant generally ranging from about 20:1 to 4:1 and preferably about 10:1 to 5:1. At these levels of the anti-foaming agent, the total phosphorus content in the composition will generally and preferably be no more than 0.01 weight percent, based on the total composition.

Where it is desired to totally exclude phosphorus any of the known, bleach-compatible silicone anti-foaming agents can be used.

In the preferred thickened LADD compositions of this invention, thickening is provided by inorganic, water-swelling colloid-forming clays of smectite and/or attapulgite types. These materials may generally be used in amounts of about 0.1 to 10 preferably 1 to 5, weight percent, to confer the desired properties. However, in the presence of the fatty acid or fatty acid metal salt stabilizers, lesser amounts of the inorganic colloid-forming clays of the smectite and/or attapulgite types can be used. For example, amounts of clay in the range of from about 0.1 to 3%, preferably 0.1 to 2.5%, especially 0.1 to 2%, are generally

sufficient to achieve the desired viscoelastic properties when used in combination with the fatty acid (or fatty acid salt) stabilizer, and other specified ingredients.

5 Smectite clays include montmorillonite (bentonite), hectorite, attapulgite, smectite, saponite, and the like. Montmorillonite clays are preferred and are available under tradenames, such as Thixogel (registered trademark) No. 1, and Gelwhite
10 (registered trademark) GP, H, etc., from Luthern Clay Products. Attapulgite clays include the materials commercially available under the tradename Attagel (registered trademark), i.e. Attagel 40, Attagel 50 and
15 Attagel 150 from Engelhard Minerals and Chemicals Corporation. Mixtures of smectite and attapulgite types in weight ratios of 4:1 to 1:5 are also useful herein. The thickening or suspending agents of the foregoing types are well known in the art.

Physical stability, i.e. resistance to phase
20 separation, settling, etc., of these liquid aqueous ADD compositions can be significantly improved by adding to the composition a small but effective amount of a long chain fatty acid or a metal salt thereof. Actually, under the preferred alkaline pH conditions of the LADD
25 composition, viz. pH 10.5 to 13.5, the fatty acids will be converted to the corresponding alkali metal salts.

The preferred long chain fatty acids are the higher aliphatic fatty acids having from about 8 to about 22 carbon atoms, more preferably from about 10 to
30 20 carbon atoms, and especially preferably from about 12 to 18 carbon atoms, inclusive of the carbon atom of the carboxyl group of the fatty acid. The aliphatic radical may be saturated or unsaturated and may be

straight or branched. Straight chain saturated fatty acids are preferred. Mixtures of fatty acids may be used, such as those derived from natural sources, such as tallow fatty acid, coco fatty acid, soya fatty acid, etc., or from synthetic sources available from industrial manufacturing processes.

Thus, examples of the fatty acids include, for example, decanoic acid, dodecanoic acid, palmitic acid, myristic acid, stearic acid, oleic acid, eicosanoic acid, tallow fatty acid, coco fatty acid, soya fatty acid, mixtures of these acids, etc. Stearic acid and mixed fatty acids are preferred.

The metal salts of the fatty acids may also be used and any of monovalent or polyvalent metals may be used. The monovalent metals include, for example, the alkali metals, especially sodium or potassium. Sodium salts (soaps) are especially preferred.

The preferred polyvalent metals are the polyvalent metals of Groups IIA, IIB and IIIB of the Periodic Table of the Elements, such as magnesium, calcium, aluminium and zinc, although other polyvalent metals, including those of Groups IIIA, IVA, VA, IB, IVB, VB, VIB, VIIB and VIII of the Periodic Table of the Elements can also be used. Specific examples of such other polyvalent metals include, Ti, Zr, V, Nb, Mn, Fe, Co, Ni, Cd, Sn, Sb, Bi etc. Generally, the metals may be present in the divalent to pentavalent state. Preferably, the polyvalent metal salts are used in their higher oxidation states. Naturally, for LADD compositions, as well as any other applications where the composition of the present invention will or may come into contact with articles used for the handling, storage or serving of food products or which otherwise

may come into contact with or be consumed by people or animals, the metal salt should be selected by taking into consideration the toxicity of the metal. For this purpose, the calcium and magnesium salts are especially
5 highly preferred as generally safe food additives.

Many of these metal salts are commercially available. For example, the aluminium salts are available in the triacid form, e.g. aluminium stearate as aluminium tristearate, $\text{Al}(\text{C}_{17}\text{H}_{35}\text{COO})_3$.

10 The monoacid salts, e.g. aluminium monostearate and diacid salts, e.g. aluminium distearate, and mixtures of two or three of the mono-, di- and triacid salts can be used for those metals, e.g. Al, with valences of +3, and mixtures of the mono and diacid salts can be used
15 for those metals, e.g. Zn, with valences of +2. It is most preferred that the diacids of the +2 valent metals and the triacids of the +3 valent metals, the tetraacids of the +4 metals, and the pentacids of the +5 valent metals, be used in predominant amounts.

20 The metal salts, as mentioned above, are generally commercially available but can be easily produced by, for example, saponification of a fatty acid, e.g. animal fat, stearic acid, etc., or the corresponding fatty acid ester, followed by treatment with an
25 hydroxide or oxide of the polyvalent metal, for example, in the case of the aluminium salt, with alum, alumina, etc., or by reaction of a soluble metal salt with a soluble fatty acid salt.

30 Calcium stearate, i.e. calcium distearate, magnesium stearate, i.e. magnesium distearate, aluminium stearate, i.e. aluminium tristearate and zinc stearate, i.e. zinc distearate, are the preferred polyvalent fatty acid salt stabilizers.

Mixed fatty acids, such as the naturally occurring acids, e.g. coco acid, as well as mixed fatty acids resulting from the commercial manufacturing process are also advantageously used as an inexpensive but
5 effective source of the long chain fatty acid.

In addition, the dimers or trimers of these acids can also be used.

The amount of the fatty acid or fatty acid salt stabilizers to achieve the desired enhancement of
10 physical stability will depend on such factors as the nature of the fatty acid (or its salt), the nature and amount of the clay thickener, detergent active compound, inorganic salts, other LADD ingredients, as well as the anticipated storage and shipping
15 conditions.

Generally, however, amounts of the polyvalent metal fatty acid salt stabilizing agents in the range of from about 0.02 to 1%, preferably from about 0.06 to 0.8%, especially preferably from about 0.08 to 0.4%,
20 provide the long term stability and absence of phase separation upon standing or during transport at both low and elevated temperatures as are desired for a commercially acceptable product.

Although not wishing to be bound by any particular
25 theory as to the mode of operation of the fatty acid (metal salt) stabilizers, it is hypothesized that these stabilizers, which under alkaline conditions, are anionic salts, interact with the surface of the cationic clay particles in suspension. Furthermore, depending
30 on the amounts, proportions and types of physical stabilizers and clay thickeners, the addition of the fatty acid (or its salt) not only increases physical stability but also provides a simultaneous increase in

apparent viscosity. Ratios of fatty acid (salt) to clay thickener in the range of from about 0.08-0.4 weight percent clay thickener agent are usually sufficient to provide these simultaneous benefits and, therefore, the use of these ingredients in these ratios is most preferred.

Generally, LADD effectiveness is directly related to (a) available chlorine levels; (b) alkalinity; (c) solubility in washing medium; and (d) foam inhibition. It is preferred herein that the pH of the LADD composition be at least about 9.5, more preferably from about 10.5 to 13.5 and most preferably at least about 11.5. At the relatively lower pH values, the LADD product is often too viscous, i.e. solid-like, and thus not readily fluidized under the shear-force levels created within the dispenser cup under normal machine operating conditions. In essence, the composition loses much, if not all, of its viscoelastic character. Addition of NaOH is thus often needed to increase the pH to within the above ranges, and to increase flowability properties. The presence of carbonate is also often needed herein, since it acts as a buffer helping to maintain the desired pH level. Excess carbonate is to be avoided, however, since it may cause the formation of needle-like crystals of carbonate, thereby impairing the stability, thixotropy and/or detergency of the LADD product, as well as impairing the dispensability of the product from, for example, squeeze tube bottles. Caustic soda (NaOH) serves the further function of neutralizing the phosphoric or phosphonic acid ester foam depressant when present. About 0.5 to 3 weight percent of NaOH and about 2 to 9 weight percent of sodium carbonate in the LADD

composition are typical, although it should be noted that sufficient alkalinity may often be provided by the alkali metal silicate.

5 The amount of water contained in these compositions should, of course, be neither so high as to produce unduly low viscosity and fluidity, nor so low as to produce unduly high viscosity and low flowability, viscoelastic properties in either case being diminished or destroyed. Such amount is readily
10 determined by routine experimentation in any particular instance, generally ranging from about 25 to 75 weight percent, preferably about 55 to 65 weight percent, in total, from all sources. The water should also be preferably deionized or softened.

15 Other conventional ingredients may be included in these compositions in small amounts, generally less than about 3 weight percent, such as perfume, hydrotropic agents, such as the sodium benzene, toluene, xylene and cumene sulphonates, preservatives,
20 dyestuffs and pigments, and the like, all, of course being stable to chlorine bleach compound and high alkalinity (properties of all the components). Especially preferred for colouring are the chlorinated phthalocyanines and polysulphides of aluminosilicate
25 which provide, respectively, pleasing green and blue tints. TiO_2 may be employed for whitening or neutralizing off-shades. Abrasives or polishing agents should be avoided in the LADD compositions as they may mar the surface of fine dishware, crystal and the like.

30 According to one preferred method of making these compositions, one should first dissolve or disperse all the inorganic salts, e.g. carbonate (when employed), silicate and zeolite, in the aqueous medium.

Thickening components including the carboxyl group containing polymer and clay (when present) are added last. The foam depressor (when employed) is preliminarily provided as an aqueous dispersion, as is
5 the thickening agent. The foam depressant dispersion, caustic soda (when employed) and inorganic salts are first mixed at elevated temperatures in aqueous solution (deionized water) and, thereafter, cooled, using agitation throughout. Bleach, surfactant, fatty
10 acid (or its metal salt stabilizer), polymer and thickener dispersion at room temperature are thereafter added to the cooled (25-35°C) solution. Excluding the chlorine bleach compound, total salt concentration (e.g. sodium silicate and carbonate) is generally about
15 20 to 50 weight percent, preferably about 25 to 40 weight percent in the composition.

Another highly preferred method for mixing the ingredients of the LADD formulations involves first forming a mixture of the water, foam suppressor,
20 detergent, carboxyl group containing polymer, fatty acid or salt and clay. These ingredients are mixed together under high shear conditions, preferably starting at room temperature, to form a uniform dispersion. To this premixed portion, the remaining
25 ingredients are introduced under low shear mixing conditions. For instance, the required amount of the premix is introduced into a low shear mixer and thereafter the remaining ingredients are added, with mixing, either sequentially or simultaneously.
30 Preferably, the ingredients are added sequentially, although it is not necessary to complete the addition of all of one ingredient before beginning to add the next ingredient. Furthermore, one or more of the

ingredients can be divided into portions and added at different times. Good results have been obtained by adding the remaining ingredients in the following sequence: sodium hydroxide, alkali metal carbonate, sodium silicate, aluminosilicate zeolite, bleach (preferably, sodium hypochlorite) and sodium hydroxide.

The liquid ADD compositions of this invention are readily employed in known manner for washing dishes, other kitchen utensils and the like in an automatic dishwasher, provided with a suitable detergent dispenser, in an aqueous wash bath containing an effective amount of the composition.

While the invention has been particularly described in connection with its application to liquid automatic dishwasher detergents it will be readily understood by one of ordinary skill in the art that with or without the benefits of viscoelasticity and physical stability which are obtained by the additional amounts of the alkali metal silicate and by the interaction of the clay and the fatty acid, the cleaning benefits provided by the combination of bleach stable detergent, bleach, and zeolite builder and bleach-stable, water-soluble carboxyl group containing polymer make the compositions of this invention useful as a general type liquid cleaning composition for dishes, glassware, cutlery, pots, pans and the like.

The cleaning performance, in terms of removal of a broad spectrum of food stains, of the composition of the present invention is comparable or slightly superior to that of similar alkali metal polyphosphate, e.g. sodium tripolyphosphate built detergents. For instance, in cleaning tests against various food residues, some of which were baked on, including egg,

peanut butter, tea, coffee, milk, chocolate milk, tomato juice, rice, rice/cheese mixture, white sauce, oatmeal and spinach, the LADD composition of the present invention achieved slightly better cleaning or
 5 the same cleaning for 14 to 16 food stains on various substrates (glasses, cups, cutlery, plates, pots) and only slightly worse for chocolate milk and baked rice on pots.

Furthermore, as will be shown in the example to
 10 follow, the compositions of this invention are generally superior to similar phosphate built compositions in terms of spotting and film formation.

The invention may be put into practice in various ways and one specific embodiment will be described to
 15 illustrate the invention with reference to the accompanying example.

All amounts and proportions referred to herein are by weight of the composition unless otherwise indicated.

20

Examples 1A and 1B

The following two compositions are prepared in order to compare the properties of the composition in
 25 accordance with the present invention (Example 1A) with a similar phosphate built composition used as a comparison (Example 1B).

<u>Example</u>	<u>1A</u>	<u>1B</u>
30 <u>Ingredient</u>		
Water, deionized	16.44	30.44
stearic acid	0.10	0.10
Smectite clay (Van Gel ES)	1.50	1.50

	Sodium Silicate (47.5% Solution of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4)	35.00	25.00
5	Sodium tripolyphosphate (substantially anhydrous, i.e. about 3% moisture)	----	12.00
	Sodium tripolyphosphate hexahydrate	----	12.00
	Aluminosilicate zeolite	24.00	-----
10	Sodium carbonate, anhydrous	6.00	6.00
	Sodium hypochlorite (1% available chlorine)	9.00	9.00
15	Surfactant (Dowfax 3B-2), 45% Na mono- and di-decyl disulphonate-aqueous solution)	0.80	0.80
20	Antifoaming agent (Knapsack LPKn 158, mixture of mono- and di-stearyl (C_{16} - C_{18}) alkyl esters of phosphoric acid, mole ratio about 1:1.3)		0.16
	0.16		
25	Caustic soda solution (50% NaOH)	3.00	3.00
	Sodium polyacrylate (MW=4,500)(45% solution)	4.00	-----
30		<u>100.00</u>	<u>100.00</u>

Each of the formulations of Examples 1A and 1B are tested to compare cleaning performance (buildup of

spots and films on glassware) using a Kenmore dishwasher with 100 gram of glassware using tap water temperature at 130°F (54°C) and 120 ppm hardness. The test procedure is described in ASTM D3566-79, except that only four cleaning cycles are used. The filming and spotting are evaluated according to the following scales:

Film Rating Scale

1. Best, no apparent film
2. Filming slight, becoming apparent
3. Noticeable film, increasing
4. Continued increase of significant film
5. Filming becoming excessive
6. Filming high, excessive buildup
7. Continued increase of excessive film.

Spot Rating Scale

- A. Best - no spots
- B. Very few spots apparent
- C. Distinct
- D. Significant coverage approximately 50%.

The results are shown below:

Cycle	<u>Performance Rating</u>			
	<u>Spots</u>		<u>Films</u>	
	<u>Ex 1A</u>	<u>Ex 1B</u>	<u>Ex 1A</u>	<u>Ex 1B</u>
1	A,B	B	1,2	1,2
2	A,B	B	1,2	1,2
3	A,B-B	B-C	1,2	1,2
4	B	B-C	2	2

Similar results to those described above will be obtained if the polyacrylate is replaced by methacrylic acid/maleic anhydride copolymer, e.g. Sokolan CP5.

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CLAIMS

1. An aqueous liquid low- or no-phosphorus cleaning composition comprising water, chlorine-bleach stable, water dispersible organic detergent, alkali metal silicate, chlorine bleach and detergent builder comprising a mixture of an aluminosilicate zeolite and a carboxyl group-containing, water-soluble, bleach-stable polymer.

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2. A composition as claimed in Claim 1 in which the detergent builder comprises from about 5 to about 35% by weight of the aluminosilicate zeolite and from about 0.5 to 10% by weight of the bleach stable polymer.

15

3. As composition as claimed in claim 1 or claim 2 further comprising an inorganic colloid forming clay thickener.

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4. A composition as claimed in anyone of claims 1 to 3 further comprising a C₈ to C₂₂ aliphatic carboxylic acid or salt thereof.

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5. A composition as claimed in anyone of claims 1 to 4 further comprising a bleach stable foam depressant.

6. A composition as claimed in claim 5 in which the foam depressant comprises an alkyl acid phosphate ester or an alkyl phosphonic acid ester containing one or two C₁₂-C₂₀ alkyl groups, or a mixture thereof.

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7. A composition as claimed in anyone of claims 1 to 6 which is free of phosphorus, or contains no more than 0.01% thereof.

5 8. A composition as claimed in anyone of claims 1 to 9 further comprising a silicone foam-depressant.

9. An aqueous thickened liquid automatic dishwasher detergent composition containing no more than about 0.01% by weight of phosphorus, comprising approximately by weight,

- (a) 5 to 35% aluminosilicate zeolite;
 - (b) more than 25% sodium silicate;
 - (c) 0 to 9% alkali metal carbonate;
 - 15 (d) 0.1 to 5% bleach stable, water-dispersible organic detergent active material;
 - (e) 0 to 5% bleach stable foam depressant;
 - (f) chlorine bleach compound in an amount to provide about 0.2 to 4% of available chlorine,
 - 20 (g) 0 to 3% of an inorganic colloid-forming clay thickener;
 - (h) 0 to 0.5% of an aliphatic fatty acid having from 8 to 22 carbon atoms, dimers thereof, or trimers thereof, or metal salts thereof;
 - 25 (i) 0 to 8% of sodium hydroxide;
 - (j) 0.5 to 10% of bleach-stable, water-soluble, carboxyl group-containing polymer; and
 - (k) water
- said composition having a pH of at least 9.5.

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10. A composition as claimed in anyone of the preceding claims in which the bleach stable polymer is polyacrylic acid or polyacrylate and has a molecular

weight of from about 1,000 to about 25,000.

5 11. A composition as claimed in claim 10 in which the bleach stable polymer has a molecular weight of from about 2,000 to about 10,000.

12. A composition as claimed in claim 9 or claim 10 or 11 when appendant to claim 9 comprising 0.03 to 0.5% of the said aliphatic fatty acid or salt (h).

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13. A composition as claimed in claim 13 in which the fatty acid is stearic acid or a salt thereof.

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14. A composition as claimed in claim 9 or anyone of claims 10 to 13 when appendant thereto comprising 0.1 to 3% of the said clay thickener (g).

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15. A composition as claimed in claim 14 in which the clay is a smectite clay or attapulgite clay.

16. A composition as claimed in anyone of the preceeding claims in which the chlorine bleach is sodium hypochlorite.

25

17. A composition as claimed in anyone of the preceeding claims which contain at least about 0.1 weight percent of a foam depressant.

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18. A composition as claimed in claim 17 in which the foam depressant is an alkyl acid phosphate ester or an alkyl phosphonic acid ester containing one or two C₁₂-C₂₀ alkyl groups, or a mixture thereof.

19. A composition as claimed in anyone of the preceding claims having a pH of about 10.5 to about 13.5.

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20. A composition as claimed in claims substantially as specifically described herein with reference to Example 1A.

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21. The method of cleaning soiled dishware in an automatic dishwashing machine which comprises contacting the soiled dishware in an automatic dishwashing machine in an aqueous washbath having dispersed therein an effective amount of a composition as claimed in anyone of claims 1 to 20.

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