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(54) **High alkalinity liquid automatic dishwasher detergent compositions.**

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EP 0 345 611 B1

Description

The present invention relates to built aqueous liquid automatic dishwasher detergent compositions.

Commercially available household-machine dishwasher detergents provided in powder 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.

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 pastes. Dishwasher products so provided are primarily objectionable in that they are insufficiently viscous to remain "anchored" in the dispenser cup of the dishwasher. Ideally, thixotropic cleansing compositions should be highly viscous in a quiescent state, Bingham plastic in nature, and have relatively high yield values. When subjected to shear stresses, however, such as being shaken in a container or squeezed through an orifice, they should quickly fluidize and, upon cessation of the applied shear stress, quickly revert to the high viscosity/Bingham plastic state. Stability is likewise of primary importance, i.e. there should be no significant evidence of phase separation or leaking after long standing.

The provision of automatic-dishwasher compositions in gel form having the aforescribed 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 hard-water minerals 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 chlorine-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). Cleansers approximating to the aforescribed compositions are mostly liquids or powders. Combining such ingredients in a gel 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. Thus, 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 depressor. Bleach is not disclosed. U.S. Patent 4,147,650 is somewhat similar, optionally including Cl-(hypochlorite) bleach but no organic surfactant or foam depressant. The product is described, moreover, as a detergent slurry with no apparent thixotropic properties.

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 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 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 function 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 Application GB 2,116,199A and GB 2,140,450A, both of which are assigned to Colgate-Palmolive, liquid ADD compositions are disclosed which have properties desirably characterizing thixotropic, gel-type structure and which include each of the various ingredients necessary for effective detergency within an automatic dishwasher. The normally gel-like aqueous 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 thixotropy index of about 2.5 to 10;
- 5 (h) sodium hydroxide, as necessary, to adjust pH; and
- (i) water, balance.

ADD compositions so formulated are low-foaming; are readily soluble in the washing medium and most effective at pH values best conducive to improved cleaning performance, viz, pH 10.5-14. 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. 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 metasilicate, an active chlorine compound and a thickening agent which is a foliated silicate of the hectorite type. Small amount of nonionic tensides and alkali metal carbonates and/or hydroxides may be used.

While these previously disclosed liquid ADD formulations are not subject or are subject to a lesser degree to one or more of the above-described deficiencies, it has been found that in actual practice, still further improvements in stability are required to increase the shelf-life of the product and thereby enhance consumer acceptance.

In US-A-4 752 409 (application Serial No. 903,924 filed September 5, 1986) some of the present inventors described the use of minor amounts of fatty acid metal salts, such as aluminum stearate, as antisetling additives to improve physical stability and rheological properties of clay based thixotropic aqueous liquid ADD compositions.

Although this prior application disclosed alkalinity levels to provide LADD compositions with pH's of at least 9.5, preferably at least 12.5, in actual practice these composition pH levels corresponded to pH levels in the aqueous wash bath which were substantially lower, usually below pH 11. For instance, the compositions exemplified in the examples of US-A-4 752 409 included 2.2 weight percent or 3.1 weight percent of a caustic soda solution (50% NaOH), to provide composition pH's of about 13. However, when added to the aqueous wash bath at a typical concentration level of about 10 grams per liter, the wash bath had a pH of under 11, such as 10.9.

US-A-4 752 409 was published on 21.6.1988, i.e. after the priority date (9.6.1988). The corresponding DE-A-37 29 381 was published on 10.3.1988. In all examples of DE-A-37 29 381 the dishwasher composition comprises 5% by weight of sodium carbonate.

GB-A-2 193 724 describes similar compositions. Again, in all examples the composition comprises 5% by weight of sodium carbonate.

While these prior compositions provide improved physical stability and acceptable cleaning performance it was desired to achieve still better cleaning performance. Toward this end the present inventors decided to increase the alkalinity level of the clay/fatty acid salt-containing liquid ADD compositions as disclosed in the aforementioned US-A-4 752 409.

It was discovered, and this was totally unexpected, that at the higher alkalinity levels, the decrease in available chlorine, for chlorine bleach containing compositions, was substantially reduced.

Accordingly, it is an object of the invention to provide chlorine bleach-containing liquid ADD compositions in which loss of available chlorine with time is reduced.

This object of the invention is achieved by providing an aqueous thixotropic automatic dishwasher composition comprising by weight:

- a) 5 to 35% alkali metal tripolyphosphate;
- b) 3 to 20% alkali metal silicate;
- c) 0 to 4% alkali metal carbonate;
- d) 1.0 to 4.5% alkali metal hydroxide;
- e) 0.1 to 5% chlorine bleach stable, water-dispersible organic detergent active material;
- 55 f) 0 to 5% chlorine bleach stable foam depressant;
- g) chlorine bleach compound in an amount to provide 0.2 to 4% of available chlorine;
- h) 0.1 to 10% of inorganic colloid-forming clay;
- i) 0.02 to 1% of a polyvalent metal salt of an aliphatic fatty acid having from 12 to 18 carbon atoms; and

j) water;

with the proviso that the total amount of alkali metal hydroxide and alkali metal carbonate is no more than 6.5% by weight and the total amount of alkali metal silicate and alkali metal carbonate is no more than 20% by weight, the pH of the composition being at least 12.8 and the pH of 1 liter of aqueous wash bath containing 10 g of the composition being at least 11.2.

It is known that LADD effectiveness is directly related to (a) available chlorine levels; (b) alkalinity; (c) solubility in washing medium; and (d) foam inhibition. Therefore, it has been suggested that the pH of the LADD composition be at least about 9.5, most preferably at least about 12.5. Amounts of from about 0.5 to 6 weight percent of NaOH and about 2 to 9 weight percent of sodium carbonate in the LADD composition are proposed in US-A-4 752 409.

In accordance with the present invention the types and amounts of the alkaline components are chosen so that when the composition is added to an aqueous wash bath to provide a concentration of 10 grams of composition per liter of wash bath the pH of the wash bath becomes at least 11.2, preferably at least 11.5, such as from 11.5 to 13.5, preferably 11.5 to 12.5. By operating at these higher than normal alkalinity levels the cleaning performance is improved and at the same time the rheological properties, and particularly, physical stability, are also improved. Furthermore, the benefit of reduction of loss of active chlorine is also obtained.

To achieve these high pH levels it is necessary to increase the total concentration of the alkaline components, as compared to the levels actually used in the prior known LADD compositions. Such a composition is shown as Example 4 in US-A-4 752 409:

Ingredient	Amount (A.I.) wt%
Sodium silicate (47.5% sol'n Na ₂ O/SiO ₂ = 1/2.4)	7.48
Monostearyl phosphate	0.16
Dowfax 3B-2	0.36
Thermphos NW	12.0
Thermphos N Hexa	12.0
Aluminum tristearate	0.1
Sodium carbonate, anhydrous	5.0
Caustic soda solution (50% NaOH)	3.1
Pharmagel Euroclay (Mg/Al silicate clay)	1.25
Sodium hypochlorite solution (11%)	1.0
Water	balance
pH 13 to 13.4.	

In this Example 4, the quantity of sodium hydroxide was increased from 2.2 weight percent (1.1 weight percent a.i.) to 6.2 weight percent (3.1 weight percent a.i.) with a corresponding decrease in the added water content, the sodium carbonate and sodium metasilicate levels remaining unchanged at 5.0% and 15.74% (7.48% a.i.), respectively.

Tests for cleaning performance and rheological behavior for the high alkalinity composition of Example 4 demonstrated that these compositions were superior to the control composition (2.2 weight percent caustic soda solution). However, when tested for available chlorine content, the control composition was slightly superior to the Example 4 composition. In contrast, when a high alkalinity formulation according to the invention was prepared by increasing the caustic soda concentration at the expense of sodium carbonate then not only cleaning performance and rheological properties are improved, but loss of available chlorine content, as compared to the control, is substantially reduced as well. Similarly, replacing Na₂CO₃ by additional alkali metal silicate also reduces available chlorine loss while improving cleaning performance and stabilizing rheological properties.

Therefore, in accordance with this invention, the high alkalinity is achieved in a clay-thickened, fatty acid salt stabilized, chlorine-bleach containing liquid automatic dishwasher detergent composition wherein the alkaline compounds include, on an active basis, based on the total composition, from 3 to 20 weight percent alkali metal silicate, from 1.0 to 4.5 weight percent alkali metal hydroxide, and from 0 to about 4 weight percent alkali metal carbonate, with the proviso that the total amount of alkali metal hydroxide and alkali metal carbonate is no more than 6.5 weight percent and the total amount of alkali metal silicate and alkali metal carbonate is no more than 20 weight percent, the pH of the composition being at least 12.8, and the pH of 1 liter of aqueous wash bath containing 10 grams of the composition preferably being at least

11.5. According to a particularly preferred embodiment the amounts of alkali metal silicate, alkali metal carbonate and alkali metal hydroxide are such that when the composition is diluted to 10g/liter the pH of the diluted composition is from 11.5 to 13.5.

Although the alkali metal of the alkaline compounds: silicate, carbonate and hydroxide, is preferably sodium, the corresponding potassium compounds, or mixtures of sodium and potassium compounds can also be used.

The sodium silicate, which provides alkalinity and protection of hard surfaces, such as fine china glaze and pattern, is employed in an amount ranging from 3 to 20 weight percent, preferably about 5 to 15 weight percent, in the composition. The sodium silicate is generally added in the form of an aqueous solution, preferably having $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:1.3 to 1:2.8, especially preferably 1:2.0 to 1:2.6. At this point, it should be mentioned that most of the other components of this composition, especially NaOH and sodium hypochlorite, are also often added in the form of a preliminary prepared aqueous dispersion or solution.

The liquid automatic dishwasher detergent compositions of this invention also include an alkali metal phosphate detergency builder, such as sodium tripolyphosphate (NaTPP), and this too will contribute to the pH of the composition.

The preferred NaTPP is employed in the LADD composition in a range of 8 to 35 weight percent, preferably 20 to 30 weight percent, and should preferably be free of heavy metal which tends to decompose or inactivate the preferred sodium hypochlorite and other chlorine bleach compounds. The NaTPP may be anhydrous or hydrated, including the stable hexahydrate with a degree of hydration of 6 corresponding to about 10% by weight of water or more. Especially preferred LADD compositions are obtained, for example, when using a 0.5:1 to 2:1 weight ratio of anhydrous to hexahydrated NaTPP, values of about 1:1 being particularly preferred.

In addition to or in place of part or all of the NaTPP detergency builder, other phosphorus or non-phosphorus inorganic or organic detergency builder salts can also be used in the composition. Examples of suitable detergency builders-sequestrants include, for instance, trisodium nitrilotriacetate, tetrasodiummethylenediamine tetraacetate, sodium citrate, and the corresponding potassium salts. Tetrapotassium or tetrasodium pyrophosphate can also be used. However, sodium tripolyphosphate is highly preferred where phosphorus-containing detergents are permitted.

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 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 are the alkyl phosphonic acid esters of the formula



and especially the alkyl acid phosphate esters of the formula



In the above formulas, one or both R groups in each type of ester may represent independently a C_{12} - C_{20} alkyl group. The ethoxylated derivatives of each type 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- C_{16} - C_{18} 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 0.1 to 5 weight percent, preferably 0.1 to 0.5 weight percent, of foam depressant in the composition is typical, the weight ratio of detergent active component (d) to foam depressant (e) generally ranging from about 10:1 to 1:1 and preferably 5:1 to 1:1. Other defoamers which may be used include, for example, the known silicones, such as available from Dow Chemicals. In addition, it is an advantageous feature of this invention that many of the stabilizing salts, such as the stearate salts, for example, aluminum stearate, are also effective as foam killers.

Although any chlorine bleach compound may be employed in the compositions of this invention, such as dichloro-isocyanurate, dichloro-dimethyl handantoin, or chlorinated TSP, alkali metal or alkaline earth metal, e.g. potassium, lithium, magnesium and especially sodium, hypochlorite is preferred. The composition should contain sufficient chlorine bleach compound to provide 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 0.2 to 4.0% by weight of sodium hypochlorite contains or provides roughly the same percentage of available chlorine. 0.8 to 1.6% by weight of available chlorine is especially preferred. For example, sodium hypochlorite (NaOCl) solution of from 11 to 13% available chlorine in amounts of 3 to 20%, preferably 7 to 12%, can be advantageously used.

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, sulfoxide or betaine water dispersible surfactant types are preferred, the first mentioned anionics being most preferred. They are used in amounts ranging from 0.1 to 5% preferably 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 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 C₁₂-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 R₂R¹N→O, in which each R represents a lower alkyl group, for instance, methyl, and R¹ 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 R₂R¹PO or sulfoxide RR¹SO can be employed. Betaine surfactants are typically of the structure R₂R¹N←R''COO-, in which each R represents a lower alkylene group having from 1 to 5 carbon atoms. Specific examples of these surfactants include lauryl-dimethylamine oxide, myristyl-dimethylamine oxide, the corresponding phosphine oxides and sulfoxides, and the corresponding betaines, including dodecyltrimethylammonium 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.

Thixotropic thickeners, i.e. thickeners for suspending agents which provide an aqueous medium with thixotropic properties, are known in the art and should, of course, be stable in these compositions, e.g. stable to high alkalinity and chlorine bleach compounds, such as sodium hypochlorite. Those used according to the invention comprise the inorganic, colloid-forming clays, preferably of smectite and/or attapulgite types. These materials are used in amounts of 0.1 to 10, preferably 1 to 5 weight percent, to confer the desired thixotropic properties and Bingham plastic character. However, in the presence of the metal salt fatty acid stabilizers the desired thixotropic properties and Bingham plastic character can be obtained in the presence of lesser amounts of the thixotropic thickeners. For example, amounts of the inorganic colloid-forming clays of the smectite and/or attapulgite types in the range of from 0.1 to 3%, preferably 0.1 to 2.5%, especially 0.1 to 2%, are generally sufficient to achieve the desired thixotropic properties and Bingham plastic character when used in combination with the physical stabilizer.

Smectite clays include montmorillonite (bentonite), hectorite, smectite, saponite, and the like. Montmorillonite clays are preferred and are available under the tradenames such as Thixogel (registered trademark) No. 1 and Gelwhite (registered trademark) GP, H, etc., from Georgia Kaolin Company; and ECCAGUM (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 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. Abrasives or polishing agents should be avoided in the

LADD compositions as they may mar the surface of fine dishware, crystal and the like.

The fatty acids are the higher aliphatic fatty acids having from 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 from which the polyvalent metal salt stabilizers can be formed include, for example, dodecanoic acid, palmitic acid, myristic acid, stearic acid, oleic acid, tallow fatty acid, coco fatty acid, soya fatty acid, mixtures of these acids, etc. Stearic acid and mixed fatty acids are preferred.

The preferred metals are the polyvalent metals of Groups IIA, IIB and IIIB, such as magnesium, calcium, aluminum 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 metal salts are used in their higher oxidation states. Naturally, for LADD compositions, as well as any other applications where the invention composition 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 higher preferred as generally safe food additives.

Many of these metal salts are commercially available. For example, the aluminum salts are available in the triacid form, e.g. aluminum stearate as aluminum tristearate, $\text{Al}(\text{C}_{17}\text{-H}_{35}\text{COO})_3$. The monoacid salts, e.g. aluminum monostearate and diacid salts, e.g. aluminum distearate, and mixtures of two or three of the mono-, di- and tri-acid salts can be used for those metals, e.g. Al, with valences of +3, and mixtures of the mono- and di-acid salts can be used 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.

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, followed by treatment with an hydroxide or oxide of the polyvalent metal, for example, in the case of the aluminum salt, with alum, alumina, etc., or by reaction of a soluble metal salt with a soluble fatty acid salt.

Calcium stearate, i.e. calcium distearate, magnesium stearate, i.e. magnesium distearate, aluminum stearate, i.e. aluminum tristearate, and zinc stearate, i.e. zinc distearate, are the preferred polyvalent fatty acid salt stabilizers. Mixed fatty acid metal salts, 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 effective source of the long chain fatty acid.

The amount of the fatty acid salt stabilizer to achieve the desired enhancement of physical stability will depend on such factors as the nature of the fatty acid salt, the nature and amount of the thixotropic agent, detergent active compound, inorganic salts, especially NaTPP, other LADD ingredients, as well as the anticipated storage and shipping conditions.

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

Depending on the amounts, proportions and types of physical stabilizers and thixotropic agents, the addition of the fatty acid salt not only increases physical stability but also provides a simultaneous increase in apparent viscosity. According to one embodiment of the invention the composition contains from 0.1 to 0.5 % of the metal salt of an aliphatic fatty acid and from 0.1 to 2 % by weight of the colloid-forming clay. Ratios of fatty acid salt to thixotropic agent in the range of from about 0.08-0.4 weight percent fatty acid salt and from about 1-2.5 weight percent thixotropic agent are usually sufficient to provide these simultaneous benefits and, therefore, the use of these ingredients in these ratios is most preferred.

The amount of water contained in these composition 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, thixotropic properties in either case being diminished or destroyed. Such amount is readily determined by routine experimentation in any particular instance, generally ranging from about 30 to 75 weight percent, preferably about 35 to 65 weight percent. The water should also be preferably deionized or softened.

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

medium. Thickening agent is added last. The foam depressor (when employed) is preliminarily provided as an aqueous dispersion, as is 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 acid metal salt stabilizer and thickener dispersion at room temperature are thereafter added to the cooled (25-35 °C) solution. Excluding the chlorine bleach compound, total salt concentration (NaTPP, sodium silicate and carbonate) is generally about 20 to 50 weight percent, preferably about 30 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, detergent, physical stabilizer (fatty acid salt) and thixotropic agent, i.e. 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 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. 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, alkali metal tripolyphosphate (hydrated), alkali metal tripolyphosphate (anhydrous or up to 5% water), bleach (preferably, sodium hypochlorite) and sodium hydroxide.

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, 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 coloring are the chlorinated phthalocyanines and polysulphides of aluminosilicate which provide, respectively, pleasing green and blue tints. TiO₂ may be employed for whitening or neutralizing off-shades.

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, generally sufficient to fill or partially fill the automatic dispenser cup of the particular machine being used.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

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

Example 1

In order to demonstrate the effect of the alkalinity of the fatty acid metal salt stabilized, clay thickened liquid ADD formulations, compositions as shown in Table 1 are prepared with varying amounts of alkaline compounds.

Table I

Ingredient	Amount (Weight/%)					
	Control	Run No. 1	Run No. 2	Run No. 3*	Run No. 5	Run No. 6
Water, deionized	41.75	41.75	41.75	37.75	38.05	34.24
Caustic soda, sol'n (50% NaOH)	2.20	5.20	7.20	6.20	2.20	2.20
Na ₂ CO ₃	5.00	2.00	-----	5.00	-----	-----
Na ₂ O·SiO ₂	15.74	15.74	15.74	15.74	15.74	-----
(47.5% sol'n, Na ₂ O:SiO ₂ =1:2.4)	-----	-----	-----	-----	8.70	-----
(57.5% sol'n, Na ₂ O:SiO ₂ =1:2.4)	-----	-----	-----	-----	-----	28.25
(55.9% sol'n, Na ₂ O:SiO ₂ =1:2)	12.00	12.00	12.00	12.00	12.00	12.00
Sodium tripolyphosphate, anhydrous	12.00	12.00	12.00	12.00	12.00	12.00
Sodium tripolyphosphate, hexahydrate	9.00	9.00	9.00	9.00	9.00	9.00
Sodium hypochlorite (11% available chlorine)	0.16	0.16	0.16	0.16	0.16	0.16
Monostearyl phosphate	0.80	0.80	0.80	0.80	0.80	0.80
Dowfax 3B-2 (45% Na monodecyl/didecyl diphenyl oxide disulfonate-aqueous solution)	0.10	0.10	0.10	0.10	0.10	0.10
Aluminum tristearate	1.25	1.25	1.25	1.25	1.25	1.25
Pharmagel H, clay	100.00	100.00	100.00	100.00	100.00	100.00
Total	10.9	11.4	11.7			
pH of 10g/liter						

* Comparative Run

In preparing these formulations, the monostearyl phosphate foam depressant and Dowfax 3B-2 detergent active compound are added to the mixture just before the Pharmagel H clay thickener; all of the NaOH is added after the clay.

The resulting liquid ADD formulations as shown in Table I are measured for cleaning performance (Table II); and for density, and physical stability (phase separation) on standing and in a shipping test. The results are shown in Table III.

EP 0 345 611 B1

Table II

Composition Run No.	CLEANING PERFORMANCE	
	AVERAGE RATING ON MIXED SOILS	AVERAGE RATING ON STARCHY SOILS ²⁾
1	5.71	3.80
2	5.85	4.00
CONTROL	5.12	3.50
POWDER ¹⁾	6.11	4.61

¹⁾ Commercially available powdery ADD, pH = 12.2

²⁾ Dishes with rice and cutlery with rice and porridge

Table III

Composition Run No.	Density g/cm ³	Unshaken liquid separation measured after 12 weeks								Shipping Test 2) % Separation (by weight)	
		Glass Bottle (% height)		Ct Type Bottle (% in weight)				100 Days 1)			
		4°C	RT ³)	35°C	43°C	4°C	RT ³)		35°C		43°C
1	1.27		0	0	0	0.2	<0.1	0.4	0.5	1±0.5	0.7
2	1.27	<2	0	0	0	1.4	0.3	3.0	5.0	1±0.5	0.7
3*	1.30	<2	0	0	0	0	0	0	0	0	0
5	1.30	0	0	0	0	0	0	0	0	0	0
6	1.28	3	0	0	0	0	0	0	0	0	0

1) Average measurement with 5 different CT bottles

2) Liquid separation measured after 6 weeks and 3000 kms in a private car in plastic bottles

3) Room temperature = 20±2°C

* Comparative Run

Example 2

The control composition and the compositions of Run Nos. 3 and 5 were aged at 4°C, room temperature (RT), 35°C or 43°C and the viscosity of each sample was measured after storage in a plastic

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Viscosity (kps)

Composition Run No.	Temp (°C)		viscosity (mpa)													
	4				RT				35				43			
	2	4	6	12	2	4	6	12	2	4	6	12	2	4	6	12
CONTROL	19	23	25	29	24	34	53	70	36	48	--	68	--	74	120	180
** 3	25	27	26	18	30	48	28	23	40	23	22	31	38	24	28	18
5	28	23	17	20	27	12	20	15	18	20	18	25	26	20	29	24

*** Comparative Run**

Example 3

The Control composition and the compositions of Run Nos. 3 and 5 and a referent example in which the aluminum stearate of the control composition was omitted and the amount of clay increased to 2% were tested to measure rheological properties after standing at room temperature for 10 days, 6 weeks and 3 months. The results are shown in Table V.

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Table V

Composition	Ageing Time	Low Shear 3 rpm		High Shear 30 rpm		Thixotropy (Pa/S)	Apparent Viscosity		
		σ_0 (Pa)	η_1 (Pa·S)	σ_0 (Pa)	η_1 (Pa·S)		1.58 S ⁻¹ (Pa·S)	25 S ⁻¹ (Pa·S)	1585 (Pa·S)
Reference	10 days	--	--	--	--	--	--	--	--
	6 weeks	6.2	28.9	34.0	0.014	766	21.5	1.65	0.33
	3 months	6.3	21.1	19.0	0.007	269	15.6	0.93	0.19
Control	10 days	6.9	35.1	34.0	0.001	1665	22.6	1.47	0.24
	6 weeks	--	--	--	--	--	--	--	--
	3 months	5.6	33.6	33.7	0.001	1450	22.2	1.42	0.23
Run No. 3*	10 days	6.6	41.4	38.7	0.012	1971	23.0	1.86	0.34
	6 weeks	6.8	37.9	39.2	0.013	1938	21.2	1.89	0.35
	3 months	7.4	28.0	35.2	0.017	1397	18.1	1.73	0.35
Run No. 5	10 days	7.5	30.8	37.5	0.003	1665	21.2	1.66	0.29
	6 weeks	7.1	31.8	341.1	0.008	1538	19.9	1.58	--
	3 months	6.3	21.7	31.6	0.008	1215	16.4	1.43	0.28

* Comparative Run

Example 4

Using the control composition, and the compositions of Run Nos. 1, 3 and 5 the available chlorine levels remaining after storage at room temperature, 35°C and 43°C for 2, 4, 6 or 12 weeks was measured. The

results are shown in Table VI.

TABLE VI

RESIDUAL CHLORINE LEVELS (% of original)

Composition	Weeks	RT			35°C			43°C		
		2	4	6	2	4	6	2	4	6
Control		96	94	90	85	80	75	66	51	35
Run No. 1		98	96	95	--	--	92	96	74	64
Run No. 3*		91	92	89	84	78	72	57	55	30
Run No. 5		98	95	93	92	92	90	76	66	59
										33

* Comparative Run

Claims

1. An aqueous thixotropic automatic dishwasher composition comprising by weight:
 - a) 5 to 35% alkali metal tripolyphosphate;

- b) 3 to 20% alkali metal silicate;
 c) 0 to 4% alkali metal carbonate;
 d) 1.0 to 4.5% alkali metal hydroxide;
 e) 0.1 to 5% chlorine bleach stable, water-dispersible organic detergent active material;
 5 f) 0 to 5% chlorine bleach stable foam depressant;
 g) chlorine bleach compound in an amount to provide 0.2 to 4% of available chlorine;
 h) 0.1 to 10% of inorganic colloid-forming clay;
 i) 0.02 to 1% of a polyvalent metal salt of an aliphatic fatty acid having from 12 to 18 carbon atoms;
 and
 10 j) water;
 with the proviso that the total amount of alkali metal hydroxide and alkali metal carbonate is no more than 6.5% by weight and the total amount of alkali metal silicate and alkali metal carbonate is no more than 20% by weight, the pH of the composition being at least 12.8 and the pH of 1 liter of aqueous wash bath containing 10 g of the composition being at least 11.2.
- 15 2. The composition of claim 1 wherein the polyvalent metal is selected from the group consisting of Mg, Ca, Ti, Zr, V, Nb, Mn, Fe, Co, Ni, Cd, Sn, Sb, Bi, Al and Zn.
3. The composition of claim 1 wherein the metal salt of an aliphatic fatty acid is the aluminum, zinc,
 20 magnesium or calcium salt of stearic acid.
4. The composition according to any of the preceding claims wherein the Clay (h) is an attapulgite clay or a smectite clay.
- 25 5. The composition of claim 4 wherein the amount of the clay (h) is in the range of from 0.1 to 3%.
6. The composition according to any of the preceding claims which contains from 0.1 to 0.5% of the metal salt of an aliphatic fatty acid (i) and from 0.1 to 2% by weight of the colloid-forming clay (h).
- 30 7. The composition according to any of the preceding claims wherein the bleach compound (f) is sodium hypochlorite.
8. The composition according to any of the preceding claims which contains at least about 0.1% by weight of the foam depressant (e).
- 35 9. The composition of claim 8 in which the foam depressant is an alkyl acid phosphate ester, an alkyl phosphonic acid ester containing 1 or 2 C₁₂₋₂₀ alkyl groups, an ethoxylated product thereof or a mixture thereof.
- 40 10. The composition according to any of the preceding claims wherein the amount of components (b), (c) and (d) is such that when the composition is diluted to 10 g/liter the pH of the diluted composition is from 11.5 to 13.5.

Patentansprüche

- 45 1. Wäßrige, thixotrope Zusammensetzung für Geschirrspülmaschinen, die bezogen auf das Gewicht umfaßt:
- a) 5 bis 35% Alkalimetalltripolyphosphat,
 b) 3 bis 20% Alkalimetallsilikat,
 50 c) 0 bis 4% Alkalimetallcarbonat,
 d) 1,0 bis 4,5% Alkalimetallhydroxid,
 e) 0,1 bis 5% chlorbleichstabiles, in Wasser dispergierbares, organisches reinigung aktives Material,
 f) 0 bis 5% chlorbleichstabiles Schaumunterdrückungsmittel,
 g) Chlorbleichverbindung in einer Menge, um 0,2 bis 4% verfügbares Chlor zu liefern,
 55 h) 0,1 bis 10% anorganischen, kolloidbildenden Ton,
 i) 0,02 bis 1% mehrbindiges Metallsalz einer aliphatischen Fettsäure mit 12 bis 18 Kohlenstoffatomen und

- j) Wasser,
mit der Maßgabe, daß die Gesamtmenge an Alkalimetallhydroxid und Alkalimetallcarbonat nicht größer als 6,5 Gew.% ist und die Gesamtmenge an Alkalimetallsilikat und Alkalimetallcarbonat nicht größer als 20 Gew.% ist, wobei der pH der Zusammensetzung mindestens 12,8 ist und der pH Wert von einem Liter wäßrigem Spülbad, das 10 g der Zusammensetzung enthält, mindestens 11,2 ist.
2. Zusammensetzung nach Anspruch 1, bei der das mehrbindige Metall ausgewählt ist aus der Gruppe bestehend aus Mg, Ca, Ti, Zr, V, Nb, Mn, Fe, Co, Ni, Cd, Sn, Sb, Bi, Al und Zn.
 3. Zusammensetzung nach Anspruch 1, bei der das Metallsalz einer aliphatischen Fettsäure das Aluminium-, Zink-, Magnesium- oder Calciumsalz von Stearinsäure ist.
 4. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei der der Ton (h) ein Attapulgit-Ton oder ein Smectit-Ton ist.
 5. Zusammensetzung nach Anspruch 4, bei der die Menge des Tons (h) im Bereich von 0,1 bis 3% liegt.
 6. Zusammensetzung nach einem der vorhergehenden Ansprüche, die 0,1 bis 0,5 % des Metallsalzes einer aliphatischen Fettsäure (i) und 0,1 bis 2 Gew.% des kolloidbildenden Tons (h) enthält.
 7. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei der die Bleichverbindung (f) Natriumhypochlorit ist.
 8. Zusammensetzung nach einem der vorhergehenden Ansprüche, die mindestens etwa 0,1 Gew.% des Schaumunterdrückungsmittels (e) enthält.
 9. Zusammensetzung nach Anspruch 8, bei der das Schaumunterdrückungsmittel ein saurer Phosphatalkylester, ein Phosphonsäurealkylester, der 1 oder 2 C₁₂₋₂₀ Alkylgruppen enthält, ein ethoxyliertes Produkt derselben oder eine Mischung derselben ist.
 10. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei der die Menge der Komponenten (b), (c) und (d) so ist, daß der pH Wert der verdünnten Zusammensetzung, wenn die Zusammensetzung auf 10 g/Liter verdünnt ist, 11,5 bis 13,5 beträgt.

35 Revendications

1. Composition aqueuse thixotrope pour le lavage automatique de la vaisselle, comprenant en poids :
 - a) 5 à 35 % de tripolyphosphate de métal alcalin;
 - b) 3 à 20 % de silicate de métal alcalin;
 - c) 0 à 4 % de carbonate de métal alcalin;
 - d) 1,0 à 4,5 % d'hydroxyde de métal alcalin;
 - e) 0,1 à 5 % de matière active d'un détergent organique, hydrodispersible, stable en présence d'un agent de blanchiment à base de chlore;
 - f) 0 à 5 % d'un agent réduisant le moussage, stable en présence d'un agent de blanchiment à base de chlore;
 - g) un agent de blanchiment à base de chlore en une quantité fournissant 0,2 à 4 % de chlore disponible;
 - h) 0,1 à 10 % d'une argile formant un colloïde inorganique;
 - i) 0,02 à 1 % d'un sel de métal polyvalent d'un acide gras aliphatique ayant de 12 à 18 atomes de carbone; et
 - j) de l'eau;
 à la condition que la teneur totale en hydroxyde de métal alcalin et en carbonate de métal alcalin soit au plus de 6,5 % en poids et la teneur totale de silicate de métal alcalin et de carbonate de métal alcalin soit au plus de 20 % en poids, le pH de la composition étant au moins de 12,8 et le pH d'un litre de bain de vaisselle aqueux contenant 10 g de la composition étant au moins de 11,2.
2. Composition selon la revendication 1, dans laquelle le métal polyvalent est choisi parmi Mg, Ca, T, Zr, V, Nb, Mn, Fe, Co, Ni, Cd, Sn, Sb, Bi, Al et Zn.

3. Composition selon la revendication 1, dans laquelle le sel métallique d'un acide gras aliphatique est un sel d'aluminium, de zinc, de magnésium ou de calcium de l'acide stéarique.
- 5 4. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'argile (h) est une argile attapulgite ou une smectite.
5. Composition selon la revendication 4, dans laquelle la teneur en argile (h) est dans la gamme de 0,1 à 3 %.
- 10 6. Composition selon l'une quelconque des revendications précédentes, qui contient de 0,1 à 0,5 % du sel métallique d'un acide gras aliphatique (i) et de 0,1 à 2 % de l'argile formant un colloïde (h).
7. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'agent de blanchiment (f) est de l'hypochlorite de sodium.
- 15 8. Composition selon l'une quelconque des revendications précédentes, qui contient au moins environ 0,1 % en poids de l'agent réduisant le moussage (e).
- 20 9. Composition selon la revendication 8, dans laquelle l'agent réduisant le moussage est un ester alkylique d'acide phosphorique, un ester alkylique d'acide phosphonique, contenant 1 ou 2 groupes alkyle en C₁₂₋₂₀, un produit éthoxylé de ceux-ci ou un mélange de ceux-ci.
- 25 10. Composition selon l'une quelconque des revendications précédentes, dans laquelle la teneur en les composants (b), (c) et (d) est telle que lorsque la composition est diluée à 10 g/litre, le pH de la composition diluée est de 11,5 à 13,5.

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