

DISHWASHER DETERGENT COMPOSITIONS

The present invention relates to thixotropic aqueous suspensions with improved physical stability. More specifically the invention relates to the use of long chain fatty acids as thixotropic agents for forming stable gel-like liquid suspensions suitable for use as liquid automatic dishwasher detergent compositions.

The present invention specifically relates to automatic dishwashing detergent compositions having thixotropic properties, improved chemical and physical stability, and increased apparent viscosity, and which are readily dispersible in the washing medium to provide effective cleaning of dishware, glassware, china and the like.

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, moreover, generally cannot be used in automatic dishwashers due to high foam levels, unacceptably low viscosities and exceedingly high alkalinity.

Recent research and development activity has focussed 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, and moreover yield spotty residues on dishware, glassware, china and the like. 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 afore-described 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, thereby degrading the suspending or thixotropic agent and impairing its effectiveness. 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 poly-phosphates; a small amount of surfactant and a suds depressor. Bleach is not disclosed. U.S. Patent No. 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 No. 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 bouyancy 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/building 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 compositions are disclosed which have properties desirably characterizing thixotropic, gel-type structure and which include each of the various ingredients necessary for effective detergency with 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; and

(g) thixotropic thickener in an amount sufficient to provide the composition with thixotropy index of about 2.5 to 10;

(h) sodium hydroxide, as necessary to adjust pH.

5 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 10.5-13.5. The compositions are normally of gel consistency, i.e. a
10 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
15 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
20 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
25 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
30 hectorite type. Small amounts of nonionic tensides and alkali metal carbonates and/or hydroxides may be used.

The formation of organoclays by the interaction of clays (such as bentonite and hectorite) with organic

compounds such as quaternary ammonium salts, has also been described [W.S. Mardis, JAOCS, Vol. 61, No. 2, p. 382 (1984)].

5 While these previously disclosed liquid ADD formulations are not subject or 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 physical stability are required to increase the shelf-life of
10 the product and thereby enhance consumer acceptance.

In our copending British Patent Application No. 8614609, Serial No. ~~2,176,495~~ the physical stability of clay based thixotropic liquid formulations is improved by addition thereto of small amounts, for example, from
15 about 0.02% to 1% by weight, of a polyvalent metal salt of a long chain fatty acid, such as aluminium stearate.

While the combination of clay thickener and fatty acid salt stabilizer has been found to provide satisfactory long term stability, such an absence of
20 phase separation for periods up to 12 weeks and longer, the addition of clay to these formulations has several drawbacks.

For example, when using clay thickeners the order of addition of the various ingredients and the control
25 of the process conditions during formulation of the compositions is critical to obtain the desired thixotropic properties and low foam characteristics. In addition, the clay thickeners are expensive materials and can contribute significantly to the final
30 product cost to the consumer. In some cases the clay thickeners may actually interfere with overall cleaning performance.

The present invention aims to provide stable thixotropic aqueous suspensions which avoid the use of clay thickeners.

5. The present invention also aims to provide liquid ADD compositions having thixotropic properties with improved physical stability and rheological properties.

10. The present invention further aims to provide thixotropic liquid ADD compositions having reduced levels of thixotropic thickener without adversely effecting the generally high viscosities at low shear rates and lower viscosities at high shear rates which are characteristic of the desired thixotropic properties.

15. More broadly, it is an object of the present invention to provide stable aqueous thixotropic non-clay based compositions, especially liquid automatic dishwasher detergent pastes or gels, by incorporating in the clay-free aqueous suspension a minor amount of a fatty acid effective to inhibit the settling of the suspended particles and phase separation.

20. According to the present invention an aqueous gel-like thixotropic liquid cleaning composition comprises water, at least one ingredient selected from the group consisting of organic detergent, chlorine bleach, detergent builder, sequestering agent, foam inhibitors, abrasive particles and mixtures thereof, and from about 0.03 to about 0.5 per cent by weight of the total composition of a thickening agent which is a mono- or polycarboxylic acid having from 8 to 22 carbon atoms, or the dimers or trimers thereof, or alkali metal salts thereof, the said composition being free or substantially free of thickeners which are clay thixotropic thickeners.

30.

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

5. (a) 5 to 35% alkali metal polyphosphate
e.g. tripolyphosphate;
- (b) 2.5 to 40% sodium silicate;
- (c) 0 to 9% alkali metal carbonate;
- (d) 0.1 to 5% chlorine bleach stable, water
10. 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) 0.03 to 0.5% of a thickening agent which is a long chain
15. fatty acid;
- (h) 0 to 8% sodium hydroxide; and
- (i) balance water, the said composition being free or substantially free of thickeners which are clay thixotropic thickeners.
20. 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
25. LADD composition can be readily poured into the dispensing cup of the automatic dishwashing machine and will, within just a few seconds, promptly thicken to its normal gel-like or pasty state to remain securely within the dispensing cup until shear forces are again applied thereto, such as by the water spray from the
30. dishwashing machine.

- The preferred long chain fatty acids are the higher aliphatic fatty monocarboxylic acids having from 8 to 22 carbon atoms, more preferably having from 10 to 20 carbon atoms, and especially preferably from 12 to 18 carbon atoms, inclusive of the carbon atom of the carboxyl group of the fatty acid. Polycarboxylic acids can also be used. 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 which can be used as thickeners in place of clay or polymeric thickeners include, for example, decanoic acid, lauric acid, dodecanoic acid, palmitic acid, myristic acid, stearic acid, oleic acid, eicosanoic acid, tallow fatty acid, coco fatty acid, soya fatty acid and mixtures of these acids. In addition, the dimers or trimers of these acids can also be used. Stearic acid and mixed fatty acids, e.g. coco fatty acid, are preferred.

- Within the ranges of carbon chain lengths of the monocarboxylic fatty acids specified herein the viscosity of the product tends to decrease as the number of carbon atoms in the monocarboxylic fatty acid decreases. No systematic trends are observed for the dimers or trimers or polybasic carboxylic acids.

- The amount of the fatty acid thickener to achieve the desired values of thixotropy and physical stability will depend on such factors as the nature of the fatty acid, detergent active compound, inorganic salts,

especially TPP, other LADD ingredients, as well as the anticipated storage and shipping conditions.

5 Generally, however, amounts of the fatty acid thixotropic agent in the range of from about 0.03 to 0.5%, preferably from about 0.03 to 0.2%, especially preferably from about 0.03 to 0.08%, provide the 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.

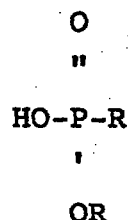
10 Generally, LADD effectiveness is directly related to (a) available chlorine levels; (b) alkalinity; (c) solubility in washing medium; and (d) foam inhibition. It is preferred herein that the pH of the LADD
15 composition be at least about 9.5, more preferably from about 10.5 to 13.5 and most preferably at least about 11.5. At relatively lower pH values, the LADD product is too viscous, i.e. solid-like, and thus not readily fluidized under the shear-force levels created within
20 the dispenser cup under normal machine operating conditions. In essence, the composition loses much, if not all, of its thixotropic 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
25 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, thixotrophy and/or detergency of the
30 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 3wt% of NaOH and about 2 to 9wt% of sodium carbonate in the LADD composition are typical, although it should be noted that sufficient alkalinity may be provided by the NaTPP and sodium silicate.

The NaTPP may be employed in the LADD composition in a range of about 8 to 35wt%, preferably about 20 to 30wt%, 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 18% by weight of water or more. Actually, in view of the stability of the hexahydrate, the presence of some water of hydration is highly effective, serving it is thought to form seeds of the stable hexahydrate which expedites hydration and solubilization of the remaining NaTPP particles. If only the hexahydrate is used, the detergent product may be too liquid and may have little if any thixotropic character. Conversely, if only the anhydrous NaTPP is used, the product may, in some cases, be too thick and, therefore, unsuitable. 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.

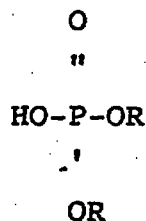
Foam inhibition is important to increase dishwasher machine efficiency and minimize destabilizing effects which might occur due to the presence of excess foam within the washer during use. Foam may be sufficiently reduced by suitable selection

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
 5 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
 10 phosphonic acid esters of the formula



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available for example from BASF--Wyandotte (PCUK-PAE),
 and especially the alkyl acid phosphate esters of the
 20 formula



25

available for example from Hooker (SAP) and Knapsack
 (LPKn-158), in which one or both R groups in each type
 of ester may represent independently a C₁₂₋₂₀ alkyl
 30 group. Mixtures of the two types, or any other
 chlorine bleach stable types, or mixtures of mono- and
 di-esters of the same type, may be employed. Especially
 preferred is a mixture of mono- and di-C₁₆₋₁₈ alkyl

acid phosphate esters such as monostearyl/distearyl acid phosphates 1.2/1 (Knapsack). When employed, proportions of 0.01 to 5 wt%, preferably 0.1 to 5wt%, preferably about 0.1 to 0.5wt%, 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 about 4:1 to 1:1. Other defoamers which may be used include for example the known silicones.

Although any chlorine bleach compound may be employed in the compositions of the invention, such as dichloro-isocyanurate, 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 silicate, which provides alkalinity and protection of hard surfaces such as fine china glaze and pattern, is employed in an amount ranging from about 2.5 to 40wt%, preferably about 10 to 35wt%, in the composition. At the higher levels specified herein for example at levels greater than about 10 wt% the

silicate also provides increased antispotting action. 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
5 of the other components of this composition, especially NaOH , sodium hypochlorite and foam depressant may also be added in the form of an aqueous dispersion or solution.

Detergent active material useful herein must be
10 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
15 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- $(\text{C}_8\text{-}_{14})$ alkyl diphenyl oxide mono and/or disulphates, commercially available for example
20 as DOWFAX (Registered Trade Mark) 3B-2 and DOWFAX 2A-1. In general, the paraffin sulphonates tend to impair, if not destroy thixotropy, having been found to unduly increase viscosity causing severe shearing force problems. In addition, the surfactant should be
25 compatible with the other ingredients of the composition. Other suitable surfactants include the primary alkylsulphates, alkylsulphonates, alkylarylsulphates and sec - alkylsulphates. Examples include sodium $\text{C}_{10\text{-}18}$ alkylsulphates such as sodium
30 dodecylsulphate and sodium tallow alcoholsulphate; sodium $\text{C}_{10\text{-}18}$ alkanesulphonates such as sodium hexadecyl-1-sulphonate and sodium $\text{C}_{12\text{-}18}$ alkylbenzenesulphonates such as sodium dodecyl-

benzenesulphonates. 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 each 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 phosphine oxides and sulfoxides, and the corresponding betaines including dodecyldimethylammonium acetate, tetra-decyldiethylammonium 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.

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, 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 25 to 75wt%,

preferably about 55 to 65wt%. The water should also be preferably deionized or softened.

5 Other conventional ingredients may be included in these compositions in small amounts generally less than about 3wt% such as perfume, hydrotropic agents such as the sodium benzene, toluene, xylene and cumene
10 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 colouring are the chlorinated phthalocyanines and polysulphides of aluminosilicate which provide, respectively, pleasing green and blue tints. TiO_2 may be employed for whitening or neutralizing off-shades.

15 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 dish washer, provided with a suitable detergent dispenser, in an aqueous wash bath containing an
20 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 the
25 benefits of thixotropy and physical stability which are obtained by the addition of the fatty acid may apply equally well to replacement of clay or polymeric thickeners in other clay or polymeric based thixotropic suspensions, such as the scouring paste formulations
30 described in the aforementioned U.S. Patent 3,985,668 dental pastes, and the like.

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

Examples 1.1 to 1.4

In order to demonstrate the effect of the fatty acid thickener, liquid ADD formulations are prepared with varying amounts of fatty acid thixotropic thickener (Examples 1.1, 1.2 and 1.3) as shown in Table 1. For comparison, a similar composition (Example 1.4) corresponding to the composition of Example 1 of GB 2,140,450A is prepared according to the procedure disclosed in the said example.

TABLE 1

Example	<u>1.1</u>	<u>1.2</u>	<u>1.3</u>	<u>1.4</u>
<u>Component</u>				
Water	32.99	32.96	32.94	41.92
5 Stearic Acid	0.03	0.06	0.08	-
Clay (Gel White GP)	-	-	-	3.00
Sodium Silicate (47.5% solution of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1:2.4)	25.00	25.00	25.00	13.73
10 Sodium tripolyphosphate (substantially anhydrous i.e. about 3% moisture)	12.00	12.00	12.00	12.00
Sodium tripolyphosphate hexahydrate	12.00	12.00	12.00	12.00
15 Sodium Carbonate (Soda Ash)	7.00	7.00	7.00	7.00
Sodium Hypochlorite (13% available chlorine)	7.61	7.61	7.61	7.61
Surfactant (Dowfax 3B-2,	0.80	0.80	0.80	0.80
20 45% Na mono- and di-decyl diphenyloxide disulphonate- aqueous solution				
Antifoaming agent (Knap-	0.16	0.16	0.16	0.16
25 sack LPKn 158, mixture of mono- and di-stearyl (C_{16} - C_{18}) alkyl esters of phosphoric acid, mole ratio about 1:1.3				
30 Caustic Soda Solution (50% NaOH)	2.40	2.40	2.40	2.40
Color (Graphitol Green)	<u>0.01</u>	<u>0.01</u>	<u>0.01</u>	<u>0.01</u>
	100.00	100.00	100.00	100.00

A sample of each of the formulations of Examples 1.2 and 2.3 and the comparative clay based formulation (Example 1.4) is subjected to the shear stress measurement using the Haake RV-3 machine as described below to determine thixotropic index and yield point. The results are shown in the attached figure (described in more detail below) where curve 1 is based on the sample of Example 1.4, curve 2 is based on the sample of Example 1.2 and curve 3 is based on the sample of Example 1.3. The value of yield point - the maximum value of shear stress, S , is shown in Table 2.

Other properties are also shown in Table 2, including the apparent viscosity, n , measured on a 24 hour old sample using a Brookfield HADT viscometer, using a No. 4 spindle at 20 rpm ($T=22^{\circ}\pm 1^{\circ}\text{C}$); density, capillary drainage rate, stability and centrifugation. Capillary drainage rate (CDR) is a measure of stability. CDR measurements are made by the following procedure: No. 1 Whatman (Registered Trade Mark) filter paper having a 6.4cm diameter circle treaced thereon is laid on a flat glass plate, 10cm x 10cm. A plastic tube, 6.4cm long, 3.4cm diameter, is placed in a standing position, centred on the circle. The tube is filled with the sample liquid ADD composition (after standing for one day). The time needed for the solvent to seep out of the tube and reach the traced circle is measured. Time is measured on three sides of the circle and averaged. Faster times mean that the gel is not successfully retaining the solvent (water) which can then leak into the filter paper. Times greater than about 7 minutes (all samples) are acceptable. The stability measurement is made by placing the sample in a glass bottle, left at room temperature, and observing the % separation at the

end of 4 weeks. The centrifugation test is also a measure of stability. Glass centrifuge tubes are filled with equal volumes of each sample and are spun vertically, i.e. in a plane parallel to the ground, in a Sorwall centrifuge, for 25 minutes at 500rpm. The volume of clear liquid is then measured. The results are reported as the ratio of the height of clear liquid to total height of sample multiplied by 100, i.e.

$$\frac{\text{height clear liquid}}{\text{total height liquid}} \times 100$$

Lower numbers indicate greater stability.

		<u>TABLE 2</u>			
		<u>1.1</u>	<u>1.2</u>	<u>1.3</u>	<u>1.4</u>
Example	Property				
	Viscosity, cps	11,460	10,660	11,260	5,100
	Yield Point, dynes/cm ²	-	372	720	392
	Density, g/ml	1.35	1.36	1.34	1.37
	CDR (minutes)	-	8.5	10.0	7.0
	Stability (4 weeks R.T.)	<1.0	0.0	0.0	5.0
	% separation				
	Centrifugation	<1.0	0.0	0.0	5.0

The data in Table 2 clearly shows the superior phase separation stability of the stearic acid based formulations as compared to the clay based formulation. These results, coupled with the thixotropy characteristics indicated by the graphical representations in the figure (to be described below)

further demonstrate the superiority of the formulations according to the present invention with respect to dishwasher cup leakage.

Example 2

- Each of the formulations of Examples 1.1 to 1.4 are tested to compare cleaning performance (build-up of spots and films on glassware) using a Kenmore (Registered Trade Mark) dishwasher using tap water temperature at 130°F (54°C) and 120ppm 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 build-up
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 in Table 3.

TABLE 3

	<u>Example</u>	<u>Performance Rating</u>	
		<u>Spot</u>	<u>Film</u>
5	1.1	B	1,2
	1.2	B,C	1,2
	1.3	B,C	2,3
	1.4	C	2,3

Example 3

10 Similar results to those described above are obtained if the stearic acid is replaced by isostearic acid, myristic acid, palmitic acid, lauric acid, Emphol dimer acid, Emphol trimer acid or Emphol 1052 polybasic acid.

15 In addition to the superior physical stability, thixotropy and cleaning performance, the compositions of the present invention have the additional significant advantage of not requiring any particular order of addition of the respective ingredients. All
20 of the ingredients can be added in any order or simultaneously to a single pot, mixer, etc., and stirred until a uniform homogeneous mixture is obtained. Mixing can be done at room temperature or at elevated temperature. It is not necessary to premix
25 any of the ingredients or to use different shear mixing conditions.

30 The invention will now be described in greater detail by way of reference to the above described specific embodiments thereof and with the aid of the following drawing in which the:

FIGURE is a graphic representation of thixotropic index of two different formulations according to the present invention and a clay thickened liquid automatic

dishwasher detergent composition as disclosed in GB 2,140,450A.

The LADD products of the prior disclosures in the
aforementioned GB 2,116,199A, GB 2,140,450A and British
5 Application No. 8614609 exhibit improved rheological
properties as evaluated by testing product viscosity of
shear rate. The compositions exhibited higher
viscosity at a low shear rate and lower viscosity at a
high shear rate, the data indicating efficient
10 fluidization and gellation well within the shear rates
extant within the standard dishwasher machine. In
practical terms, this means improved pouring and
processing characteristics as well as less leaking in
the machine dispenser-cup, compared to prior liquid or
15 gel ADD products. For applied shear rates
corresponding to 3 to 30rpm, viscosities (Brookfield)
correspondingly ranged from about 10,000 to 30,000cps
to about 3000-7000cps, as measured at room temperature
by means of an LVT Brookfield viscometer after 3
20 minutes using a No. 4 spindle. A shear rate of 7.4 sec^{-1}
corresponds to a spindle rpm of about 3. An
approximate ten-fold increase in shear rate produces
about a 3- to 9-fold reduction in viscosity. The
compositions of our prior above-mentioned invention
25 thus exhibit threshold fluidizations at lower shear
rates and of significantly greater extent in terms of
incremental increases in shear rate versus incremental
decrease in viscosity. This property of the LADD
products of the prior invention is summarized in terms
30 of thixotropic index (TI) which is the ratio of the
apparent viscosity at 3rpm and at 30rpm. The prior
compositions have a TI of from 2 to 10. The LADD
compositions should exhibit substantial and quick

return to prior quiescent state consistency when the shear force is discontinued.

5 While the determination of thixotropic index TI as a ratio of apparent viscosity at 3 and 30rpm provides a satisfactory measure of product usefulness further research and experience has shown that a more reliable measure of thixotropic index and product usefulness as a liquid ADD is provided by determining thixotropy as a measure of the area in the hysteresis loop resulting from plotting, under the conditions described below, 10 shear stress, S , as a function of shear rate, n , when the shear rate is increased from 0 to a maximum value and then returned to 0. The larger the area in the hysteresis loop, the greater is the thixotropic index. 15 In terms of apparent viscosity, it has also been ascertained that so long as the viscosity at room temperature ($22^{\circ}\pm 1^{\circ}\text{C}$) measured in a Brookfield Viscometer HADT, using a number 4 spindle at 20rpm, is less than about 20,000cps, the composition can be 20 readily be shaken so that a thixotropic composition can be easily "fluidized" or "liquefied" to allow the product to be dispensed through a conventional squeeze tube bottle or other convenient dispenser.

The present invention is based upon the surprising 25 discovery that the same or improved rheological properties and physical stability, i.e. resistance to phase separation, settling, etc., as in these prior liquid aqueous ADD compositions can be achieved, at significantly lower cost and without any particular processing requirements, by adding to the composition 30 a small but effective amount of a long chain fatty acid in place of the clay thixotropic thickener and, where used, also the metal salt of the fatty acid. At the

same time, improvements in spotting and filming performance (i.e. fewer spots and reduced filming) can be achieved.

As an example of the improvement in rheological properties over a standard clay based thixotropic liquid ADD, reference is made to the attached drawing which is a plot of shear stress, S , as a function of shear rate, n , for a clay based LADD (3 wt% clay) (curve 1) and for two similar LADD compositions in which the clay is replaced by 0.06 wt% stearic acid (curve 2) or by 0.08 wt% stearic acid (curve 3). Shear stress, S , is measured in a static experiment using a Haake RV-3 machine provided with a coaxial cup. The sample is placed in the outer cup and the inner cup is rotated by the machine at progressively higher shear rates to a maximum of 113 sec^{-1} and then the shear rate is progressively lowered to zero. The response is automatically recorded as the shear stress. The experiments were carried out using an MV II sensor system (constant values, $A=3.76 \text{ Pa}$, $M=0.9 \text{ sec}^{-1}$). The area between the resulting curved lines for each sample is a measure of thixotropy, with larger areas indicating higher thixotropy. The yield point of each sample can also be determined from the curves shown in the figure; the yield point is the maximum stress in the curve of shear stress versus shear rate. At the same time, the physical stability is such that even after six weeks or longer, over temperature ranges extending from near freezing to 40°C and more, the compositions containing the fatty acid thickeners do not undergo any visible phase separation.

CLAIMS

1. An aqueous gel-like thixotropic liquid cleaning composition comprising water, at least one ingredient selected from the group consisting of organic detergent, chlorine bleach, detergent builder, sequestering agent, foam inhibitors, abrasive particles and mixtures thereof, and from about 0.03 to about 0.5 per cent by weight of the total composition of a thickening agent which is a mono- or polycarboxylic acid having from 8 to 22 carbon atoms, or the dimers or trimers thereof, or alkali metal salts thereof, the said composition being free or substantially free of thickeners which are clay thixotropic thickeners.
- 5.
- 10.
2. An aqueous thixotropic automatic dishwasher composition comprising approximately by weight:
- (a) 5 to 35% alkali metal tripolyphosphate;
 - (b) 2.5 to 40% sodium silicate;
 - 15. (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;
 - 20. (f) chlorine bleach compound in an amount to provide about 0.2 to 4% of available chlorine;
 - (g) 0.03 to 0.5% of a thickening agent which is an aliphatic fatty acid having from 8 to 22 carbon atoms, dimers thereof, or trimers thereof;
 - 25. (h) 0 to 8% of sodium hydroxide;
- 30.



(i) balance water, the said composition being free or substantially free of thickeners which are clay thixotropic thickeners.

5. 3. A composition as claimed in Claim 2 in which the aliphatic fatty acid (g) has from 10 to 20 carbon atoms.

10. 4. A composition as claimed in Claim 3 in which the fatty acid has from 12 to 18 carbon atoms.

5. A composition as claimed in Claim 2 in which the fatty acid is stearic acid.

15. 6. A composition as claimed in any one of Claims 1 to 5 in which the fatty acid (g) is present in an amount of from about 0.03 to 0.2%.

20. 7. A composition as claimed in Claim 6 in which the fatty acid (g) is present in an amount of from about 0.03 to 0.08%.

25. 8. A composition as claimed in any one of Claims 1 to 7 in which the chlorine bleach compound (f) is sodium hypochlorite.

30. 9. A composition as claimed in any one of Claims 1 to 8 which contains at least about 0.1 wt% of the foam depressant (e).



10. A composition as claimed in Claim 9 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.
5. 11. A composition as claimed in any one of Claims 1 to 10 having a pH of about 10.5 to about 13.5.
10. 12. A composition as claimed in Claim 1 substantially as specifically described herein with reference to examples 1.1 to 1.3, 2 or 3.
15. 13. A method for 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 any one of Claims 1 to 12.
- 20.
-
- 25.
- 30.