

"THIXOTROPIC AUTOMATIC DISHWASHER
COMPOSITION WITH CHLORINE BLEACH"

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

10. 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,
15. 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,
20. 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
25. compositions, e.g. scouring cleansers and automatic-dishwasher products characterised as thixotropic pastes. Dishwasher products so provided are primarily objectionable in that they are
30. 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 proved 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
15. (1) sodium tripolyphosphate (NaTPP) to soften or tie up hard-water minerals and to emulsify and/or
 20. peptize soil; (2) sodium silicate to supply the alkalinity necessary for effective detergency and to
 25. 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)
 30. 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

5. 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
10. 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 No. 4,115,308 discloses thixotropic automatic dishwasher
15. 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 No. 4,147,650
20. 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.
25. 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
30. 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.
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20. stated. Foam killer is not disclosed.

- The present invention aims to provide a detergent composition having thixotropic properties, beneficially adapted for use in an automatic dishwasher, and not subject or subject to a lesser degree to one or more of the above-described deficiencies.
25. degree to one or more of the above-described deficiencies.

- The invention also aims to provide such a composition having good physical stability with no significant phase separation being evident after prolonged periods of standing.
30. prolonged periods of standing.

The invention also aims to provide such a composition wherein problems associated with undesired interaction of chemically active ingredients are eliminated or at least substantially mitigated.

5. The invention also aims to provide such a composition having the aforementioned stability under the highly alkaline conditions necessary for effective detergent performance.

10. The invention also aims to provide such a composition having improved rheological properties exhibiting higher viscosities at low shear rates and lower viscosities at high shear rates, thus being advantageously adapted for use in the dispenser cup of automatic dishwashing machines.

15. The invention also aims to provide such a composition having low foam characteristics, improved detergency and which is readily dispersible in the washing machine.

20. According to the broader aspects of the present invention a normally gel-like aqueous automatic dishwasher detergent composition having thixotropic properties comprises, approximately by weight:

- (a) 5 or 8 to 35% alkali metal tripolyphosphate;
- (b) 2.5 to 20% sodium silicate;
- 25. (c) 0 to 9% alkali metal carbonate,
- (d) 0.1 to 5% chlorine bleach stable, water-dispersible organic anionic, amine oxide, phosphine oxide, sulfoxide or betaine detergent active material;
- 30. (e) 0 to 5% chlorine bleach stable foam depressant,

(f) chlorine bleach compound in an amount to provide about 0.2 to 4%, preferably 0.2 to 2% of available chlorine; and

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

10. ADD compositions so formulated are low-foaming; stable, both chemically and physically; 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 highly viscous, opaque jelly-like material having Bingham plastic character and thus relatively high yield values.
15. 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
20. dispersed. When the shear force is discontinued, the fluid composition quickly reverts to a high viscosity, Bingham plastic state closely approximating its prior consistency.

25. Generally, ADD 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 ADD composition be at least about 9.5, more preferably from about 10.5-13.5 and most preferably
30. at least about 11.5. At relatively lower pH values, the ADD product is 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
5. 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 needed herein, since it acts as a buffer helping to maintain the
10. 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 ADD product. Caustic soda (NaOH)
15. serves the further function of neutralizing the phosphoric or phosphonic acid ester foam depressant when present. About 0.5 to 3 wt % of NaOH and about 2 to 9 wt % of sodium carbonate in the composition are typical although it should be noted that
20. sufficient alkalinity may be provided by the NaTPP and sodium silicate.

- The NaTPP employed in the composition in a range of about 8 to 35 wt %, preferably about 20 to 30 wt %, should preferably be free of heavy metal which
25. tends to decompose or inactivate the preferred sodium hypochlorite and other chlorine bleach compounds. The NaTPP may have an average degree of hydration of less than about 1 or more than about 5 e.g. 0 to 2.7% by weight or at least 16.5% of water,
30. including the stable hexahydrate with a degree of

hydration of 6 corresponding to about 18% by weight of water or more. Actually, humidification to an average of about 0.3 to 1% water is highly effective, serving it is thought to form seeds of the stable hexahydrate which expedites hydration and solubilization of the remaining NaTPP particles.

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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

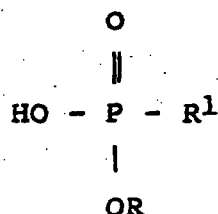
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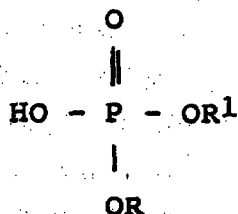
wash water in the machine whereby suitable adjustment of the proportions of NaTPP which has a water-softening effect may aid in providing the desired degree of foam inhibition. However, it is generally preferred to include a chlorine bleach stable foam depressant or inhibitor. Particularly effective are the alkyl phosphonic acid esters of the formula

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



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available for example from Hooker (SAP) and Knapsack (LPKn-158), in which R or R¹ or both in each type of ester may represent independently a C₁₂₋₂₀ alkyl group, and when only one of such R and R¹ groups

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represents a C₁₂₋₂₀ alkyl group, the other represents a hydrogen atom. Mixtures of the two types, or any other chlorine bleach stable types, or mixture of mono- and di-esters of the same type, may be employed. Especially preferred is a mixture of mono- and di-

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C₁₆₋₁₈ alkyl acid phosphate esters such as mono-stearyl/distearyl acid phosphates 1.2/1 (Knapsack).

When employed, proportions of 0.1 to 5 wt %, preferably about 0.1 to 0.5 wt %, of foam depressant in the composition is typical, the weight ratio of

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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.

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Although any chlorine bleach compound may be employed in the compositions of this 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

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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.

- 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 20 wt %, preferably about 5 to 15 wt %, in 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. At this point it should be mentioned that most of the other components of this composition, especially NaOH, sodium hypochlorite, foam depressant and thixotropic thickener, are also often added in the form of a preliminarily prepared aqueous dispersion or solution.

- Detergent active material useful herein must be stable in the presence of chlorine bleach, especially hypochlorite bleach, and preferably comprise those of the organic anionic, amine oxide, phosphine oxide, sulphoxide or betaine water-dispersible surfactant types, the first mentioned anionics being most preferred. They are used in amounts ranging from about 0.1 to 5% preferably about 0.5 to 2.0%, more preferably about 0.3 to 0.8%. Particularly preferred surfactants herein are

- the linear or branched alkali metal mono- and/or di-(C₈-14) alkyl diphenyl oxide mono- and/or disulphonates, commercially available for example 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 compatible with the other ingredients of the composition. Other suitable surfactants include the primary alkylsulphates, alkylsulphonates, alkylarylsulphonates and sec.-alkylsulphates. Examples are sodium C₁₀-C₁₈ alkylsulphates such as sodium dodecylsulphate and sodium tallow alcohol-sulphate; sodium C₁₀-C₁₈ alkanesulphonates such as sodium hexadecyl-1-sulphonate; and sodium C₁₂-C₁₈ alkylbenzenesulphonates such as sodium dodecylbenzenesulphonate. 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 represent 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 sulphoxide 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 lauryl-dimethylamine oxide, myristyldimethylamine oxide, the corresponding phosphine oxides and sulphoxides, and the corresponding betaines including dodecyldimethylammonium acetate, tetradecyl-diethylammonium 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 or suspending agents which provide an aqueous medium with thixotropic properties, are known in the art and may be organic or inorganic water soluble, water-dispersible or colloid-forming, and monomeric or polymeric, and should of course be stable in these compositions, e.g. stable to high alkalinity and chlorine bleach compounds such as sodium hypochlorite. Those specially preferred generally comprise the inorganic, colloid-forming clays of smectite and/or attapulgite types. These materials are generally used in amounts of about 1.5 to 10 preferably 2 to 5 wt % but in any event in an amount sufficient to confer the desired thixotropic properties and Bingham plastic character.

- Smectite clays include montmorillonite (bentonite), hectorite, saponite, and the like.

Materials of this type are available under trade names such as Thixogel (Registered Trade Mark) No. 1 and Gelwhite (Registered Trade Mark) GP from Georgia Kaolin Company (both being montmorillonites).

5. Attapulgite clays include the materials commercially available under the trade name Attagel (Registered Trade Mark), i.e. Attagel 40, Attagel 50 and Attagel 150 from Engelhard Minerals and Chemicals Corporation. mixtures of smectite and attapulgite
10. types in weight ratios of 4:1 to 1:5 are also useful herein. Thickening or suspending agents of the foregoing types are well known in the art, being described, for example, in U.S. Patent No. 3,985,668 referred to above. Abrasives or polishing agents
15. should be avoided.

- 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
20. 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 45 to 75 wt %, preferably about 55 to 65 wt %. The
 25. water should also be preferably deionized or softened.

- The ADD product of this invention exhibits improved rheological properties as evaluated by testing product viscosity as a function of shear
30. rate. Investigation confirms the compositions to

- exhibit higher viscosity at a low shear rate and lower viscosity at a high shear rate the data indicating efficient fluidization and gellation well within the shear rates extant within the dishwasher machine. In practical terms, this means improved pouring and processing characteristics as well as less leaking in the machine dispenser-cup, compared to current liquid or gel ADD products. For applied shear rates corresponding to 3 to 30 rpm,
5. viscosities (Brookfield) correspondingly range from about 15,000-30,000 cps to about 3000-5000 cps, as measured at room temperature by means of an LVT Brookfield viscometer after 3 minutes using a No.4 spindle. A shear rate of 7.4 sec^{-1} corresponds to a
10. spindle rpm of about 3. An approximate ten-fold increase in shear rate produces a six- to seven-fold reduction in viscosity. With current ADD gels, the corresponding reduction in viscosity is only about
15. two-fold. Moreover, with such compositions, the initial viscosity taken at about 3 rpm is only about
20. 2500-2700 cps. The compositions of the present invention thus exhibit threshold fluidizations at lower shear rates and of significantly greater extent in terms of incremental increases in shear
25. rate vs incremental decrease in viscosity. This property of the ADD products of the present invention is summarized in terms of a thixotropic index (TI) which is the ratio of the apparent viscosity at 3 rpm and at 30 rpm. The present
30. compositions have a TI of from 2.5 to 10 and preferably 6 to 8. Each of the ADD compositions

tested exhibited substantial and quick return to prior quiescent state consistency when the shear force was discontinued.

- According to one preferred method of making
5. 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
 10. 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,
 15. using agitation throughout. Bleach, surfactant 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)
 20. is generally about 20 to 50 wt %, preferably about 30 to 40 wt %, in the composition.

- Other conventional ingredients may be included in these compositions in small amounts generally less than about 3 wt % such as perfume, hydrotropic
25. 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 compounds and high alkalinity (properties of all the components). Especially
 30. preferred for colouring are the chlorinated phthalo-

cyanines and polysulphides of aluminosilicate which provide, respectively, pleasing green and blue tints. TiO_2 may be employed for whitening or neutralizing off-shades.

5. 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
10. containing an effective amount of the composition.

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.

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

EXAMPLE 1

20. A preliminary dispersion of 0.16 g of foam suppressor, comprising a 2:1 mixture of mono- and di- (C_{16} - C_{18}) alkyl esters of phosphoric acid, Knapsack LPKn158, in 6g water was prepared by mixing at 60°C for 30 minutes using a disk impeller. This dispersion is designated Part 1.

25. A preliminary dispersion of 3g of GELWHITE GP (hydration) thickener in 17g water was prepared by mixing at 70°C for 10 minutes using a Z-Blade mixer. This dispersion is designated Part 2.

30. The following ingredients were mixed in a Giusti (Registered Trade Mark) mixer at 50-60°C:

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	<u>%</u>	<u>% of active ingredient (AI)</u>
Deionized water	16.9	
5. Part I	6.16	0.16
Caustic soda solution (49% NaOH)	2.40	1.2
Sodium carbonate	7.00	7.0
10. Sodium silicate, 47.5% solution of Na ₂ O:SiO ₂ ratio of 1:2.4	13.74	6.5
Sodium TPP (substantially anhydrous - i.e. 0-5%, especially 3%, moisture)	12.00	11.54
15. Sodium TPP (hexahydrate)	12.00	9.36

The mixture was cooled to 25-30°C and agitation maintained throughout, and the following ingredients at room temperature were added thereto:

	<u>%</u>	<u>AI %</u>
20. Sodium hypochlorite solution (13% available chlorine)	7.615	1.0
Part 2 (dispersed with a highspeed turbine)	20.00	3.0
25. Dowfax 3B-2 (45% Na monodecyl/ didecyl diphenyl oxide di- sulphonates as an aqueous solution)	0.80	0.36
Total water		58.5

30. An opaque composition (about 40% AI) having a

- gel-like consistency was obtained. The composition was determined to have a TI of about 7, according to the procedure hereinbefore described, based upon apparent viscosity values of 28,000 cps and 4,000 cps at 3 rpm and 30 rpm respectively using a Brookfield viscometer with No.4 Spindle. When tested in an automatic dishwasher apparatus provided with a suitable dispenser cup, the above composition provided excellent cleaning performance and was easily and quickly dispensed. The composition was observed to be satisfactorily nonfoaming. Little or no phase separation was observed after prolonged standing in a closed container. The pH of the composition, measured as a 1% solution in water, was 11.6. When conducting the shear-test evaluations, it was observed that the compositions quickly reverted to its prior quiescent state consistency, suggesting no appreciable loss of yield value when tested within the limits hereinbefore described, i.e. within shear-force limiting values at least approximately those extant within an energized automatic dishwasher. No discernible differences were observed when the ADD product was dispensed by squeeze tube rather than by dispenser cup.

25. EXAMPLE 2

- Example 1, illustrating a combined polyphosphate carbonate silicate concentration of about 37% was repeated, but varying the total concentration of such salts within the limits previously given. Best results were obtained at a combined-salt concentration of at least 30% and particularly when the

- sodium tripolyphosphate concentration was at least about 20%. Higher silicate concentrations, desirable to protect china glaze and patterns, also impart higher alkalinity which can be compensated for by appropriately reducing the caustic soda concentration and/or adjusting the sodium carbonate (buffer) concentration. The composition appears to be most sensitive from the point of view of the results to variations in the NaTPP concentration (the higher concentration range is more effective) as well as its degree of hydration. Variations in surfactant concentration generally require corresponding and direct variations in foam-suppressor concentration to achieve the desired low-foam levels.

- Decrease of the pH of the composition of Example 1 below about 10.5 is accompanied by significant decrease in effectiveness, as well as a corresponding decrease of flowability of the composition.

EXAMPLE 3

- Similar results were obtained when the procedure of Example 1 was repeated, but certain ingredients were varied namely replacing the Dowfax with an alkyl sulphate surfactant, e.g. sodium coconut alkyl sulphate, and the Gelwhite with an attapulgite clay, e.g. Attagel 50; or a 2:1 mixture of montmorillonite and Attagel 50.

EXAMPLE 4

- The addition of small amounts, e.g. 0.002-0.05%

- of chlorinated phthalocyanine and aluminosilicate dyes respectively to the Example 1 composition (included with the preliminary thickener dispersion or post-added to the cooled solution) produces pleasantly coloured green and blue compositions respectively.

EXAMPLE 5

- In this example, the ingredients are added with agitation to the mixing vessel in sequence in order as listed with final homogenation:

	<u>Parts (wt)</u>	<u>AI %</u>
Deionized water	39.463	
2% Green colour solution	0.173	0.003
Attagel 50 clay thickener	3.375	3.375
15. (attapulgate)		
Titanium dioxide - Anatase	0.375	0.375
Na ₅ TPP - 0.5% moisture		
(1/2 total)	11.558	11.501
<u>Foam depressant</u>		
20. Knapsack LPKn158	0.160	0.160
Sodium hypochlorite solution		
(13% available chlorine, approx.)	9.230	1.20
Sodium carbonate	3.000	3.0
25. 47.5% Sodium silicate solution		
of Na ₂ O:SiO ₂ ratio of 1:2.4	17.895	8.50
49% Sodium hydroxide solution	2.600	1.27
Na ₅ TPP - 0.5% moisture	11.558	11.501
<u>Detergent active surfactant</u>		
30. Dowfax 3B-2	0.800	0.36

	<u>Standards</u>	<u>Parts (wt)</u>	<u>AI %</u>
	Total Moisture	59.5%	
	Available chlorine	1.2% + or - 0.1%	
5.	Silicates	8.5%	
	pH	12.8 + or - 0.3	
	Specific gravity	1.35 Min.	
	Viscosity (Brookfield RVF, No.5 Spindle, 20 RPM for 20 rev. at 25°C)	9,250 + or - 3,250 cps.	
10.	Our copending application No. 83.01299 claims aqueous automatic dishwasher compositions comprising approximately by weight: (a) 5 to 35% water-soluble alkali metal tripolyphosphate having an average degree of hydration of about 1 to 5; (b) 2.5 to 20% sodium silicate; (c) 0 to 9% water-soluble alkali metal carbonate; (d) 0.1 to 5% bleach stable, water-dispersible organic surfactant; (e) 0.1 to 0.5% of a mono- or di- or mono- and di-(C ₁₆ -C ₁₈) alkyl ester of phosphoric acid as a foam suppressor; (f) 3-20% of sodium hypochlorite solution containing 13% available chlorine; (g) 1.5 to 10% inorganic, colloid-forming clay thickener; and (h) sufficient sodium hydroxide to provide a pH of 10.5 to about 13.5, the amount of phosphoric acid ester being sufficient to provide low-foaming characteristics, the amount of sodium hydroxide being at least sufficient to neutralize the said phosphoric acid ester, and the composition having a thixotropy index (as defined herein) of about 2.5 to 10.		
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We make no claim to such compositions herein. Subject to such disclaimer what we claim is set out in the appended claims.

5. In a narrower aspect of the present invention we make no claim to compositions for which the sodium tripolyphosphate prior to addition to the composition had a degree of hydration of 1 to 5.

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CLAIMS

1. An aqueous thixotropic automatic dishwasher composition comprising approximately by weight:
 - (a) as ingredient A, 5 to 35% alkali metal tripolyphosphate;
 5. (b) as ingredient B, 2.5 to 20% sodium silicate;
 - (c) optionally, as ingredient C, 0 to 9% alkali metal carbonate;
 - (d) as ingredient D, 0.1 to 5% chlorine bleach stable, water-dispersible organic anionic, amine
 10. oxide, phosphine oxide, sulphoxide or betaine detergent active material;
 - (e) optionally, as ingredient E, 0 to 5% chlorine bleach stable foam depressant;
 - (f) as ingredient F, chlorine bleach compound in
 15. an amount to provide about 0.2 to 4% of available chlorine;
 - (g) as ingredient G, thixotropic thickener in an amount sufficient to provide the composition with a thixotropy index of about 2.5 to 10; and
 20. (h) optionally, as ingredient H, 0 to 3% of sodium hydroxide.
2. A composition as claimed in Claim 1 in which ingredient F, the chlorine bleach compound, is sodium
25. hypochlorite.
3. A composition as claimed in Claim 1 or Claim 2 which contains at least about 0.1 wt % of ingredient E, the foam depressant.
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4. A composition as claimed in Claim 3 in which, ingredient E, the foam depressant, is an alkyl acid phosphate ester or an alkyl phosphonic acid ester containing one or two C₁₂₋₂₀ alkyl groups, or a mixture thereof.
5. A composition as claimed in any one of Claims 1 to 4 having a pH of 10.5 to about 13.5.
10. 6. An aqueous thixotropic automatic dishwasher composition comprising approximately by weight:
 - (a) as ingredient A, 8 to 35% alkali metal tripolyphosphate which prior to addition to the composition had a degree of hydration of less than 1;
 15. (b) as ingredient B, 2.5 to 20% sodium silicate;
 - (c) optionally, as ingredient C, 0 to 9% alkali metal carbonate;
 - (d) as ingredient D, 0.1 to 5% chlorine bleach stable, water-dispersible organic anionic, amine
 20. oxide, phosphine oxide, sulfoxide or betaine detergent active material;
 - (e) optionally, as ingredient E, 0 to 5% chlorine bleach stable foam depressant;
 - (f) as ingredient F, chlorine bleach compound
 25. in an amount to provide about 0.2 to 4% of available chlorine;
 - (g) as ingredient G, thixotropic thickener in an amount sufficient to provide the composition with a thixotropy index of about 2.5 to 10; and
 30. (h) optionally, as ingredient H, 0 to 3% of sodium hydroxide.



7. An aqueous thixotropic automatic dishwasher composition comprising approximately by weight:
- (a) as ingredient A, 8 to 35% alkali metal tripolyphosphate which prior to addition to the composition had a degree of hydration greater than 5;
 - (b) as ingredient B, 2.5 to 20% sodium silicate;
 - (c) optionally, as ingredient C, 0 to 9% alkali metal carbonate;
 - (d) as ingredient D, 0.1 to 5% chlorine bleach stable, water-dispersible organic anionic, amine oxide, phosphine oxide, sulphoxide or betaine detergent active material;
 - (e) optionally, as ingredient E, 0 to 5% chlorine bleach stable foam depressant;
 - (f) as ingredient F, chlorine bleach compound in an amount to provide about 0.2 to 4% of available chlorine;
 - (g) as ingredient G, thixotropic thickener in an amount sufficient to provide the composition with a thixotropy index of about 2.5 to 10; and
 - (h) optionally, as ingredient H, 0 to 3% of sodium hydroxide.

8. A composition as claimed in Claim 6 or Claim 7 in which, ingredient E, the foam depressant, is an alkyl phosphonic acid ester containing one or two C₁₂-20 alkyl groups, or a mixture thereof.

9. A composition as claimed in Claim 6 or Claim 7 in which ingredient E, the foam depressant, is an alkyl acid phosphate ester containing one or two C₁₂-15 or C₁₇-20 alkyl groups, or a mixture thereof.



26.

10. A composition as claimed in any one of Claims 6 to 9 in which ingredient F, the chlorine bleach compound, is other than sodium hypochlorite.
5. 11. A composition as claimed in any one of Claims 6 to 10 which contains less than 0.1 wt % of ingredient E, the foam depressant.
10. 12. A composition as claimed in any one of Claims 6 to 11 having a pH of 10.5 to about 13.5, but containing no sodium hydroxide.
15. 13. An aqueous thixotropic automatic dishwasher composition comprising, approximately by weight;
- (a) as ingredient A, 8 to 35% alkali metal tri-polyphosphate which prior to addition to the composition had a degree of hydration of less than 1;
- (b) as ingredient B, 2.5 to 20% sodium silicate;
- (c) as ingredient C, 2 to 9% sodium carbonate;
20. (d) as ingredient D, 0.1 to 5% chlorine bleach stable, water-dispersible organic anionic, amine oxide, phosphine oxide, sulphoxide or betaine detergent active material;
- (e) optionally, as ingredient E, 0 to 5% chlorine bleach stable foam depressant;
25. (f) as ingredient F, sodium hypochlorite in an amount to provide about 0.2 to 2% of available chlorine;
- (g) as ingredient G, 1.5 to 10% thixotropic smectite and/or attapulgite clay thickener sufficient to provide the composition with a thixotropy index of about 2.5 to 10; and
- 30.



(h) as ingredient H, sodium hydroxide in an amount sufficient to provide the composition with a pH of about 10.5 to 13.5.

5. 14. An aqueous thixotropic automatic dishwasher composition comprising, approximately by weight;
- (a) as ingredient A, 8 to 35% alkali metal tri-polyphosphate which prior to addition to the composition had a degree of hydration greater than 5;
10. (b) as ingredient B, 2.5 to 20% sodium silicate;
- (c) as ingredient C, 2 to 9% sodium carbonate;
- (d) as ingredient D, 0.1 to 5% chlorine bleach stable, water-dispersible organic anionic, amine oxide, phosphine oxide, sulphoxide or betaine
15. detergent active material;
- (e) as ingredient E, 0 to 5% chlorine bleach stable foam depressant;
- (f) as ingredient F, sodium hypochlorite in an amount to provide about 0.2 to 2% of available
20. chlorine;
- (g) as ingredient G, 1.5 to 10% thixotropic smectite and/or attapulgite clay thickener sufficient to provide the composition with a thixotropy index of about 2.5 to 10; and
25. (h) as ingredient H, sodium hydroxide in an amount sufficient to provide the composition with a pH of about 10.5 to 13.5.

15. A composition as claimed in any one of
30. Claims 1 to 14 containing about 0.5 to 2% of ingredient D, the detergent active material.



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5. 16. A composition as claimed in any one of Claims 1 to 15 in which ingredient D, the detergent active material, is a mixture of two or more organic anionic, amine oxide, phosphine oxide, sulfoxide or betaine surfactants.

10. 17. A composition as claimed in any one of Claims 1 to 15 in which ingredient D is an organic anionic surfactant.

15. 18. A composition as claimed in any one of Claims 1 to 15 in which ingredient D, the detergent active material, is an organic anionic alkali metal sulphate or sulphonate.

20. 19. A composition as claimed in any one of Claims 1 to 15 in which ingredient D, the detergent active material, is an alkali metal C₈₋₁₄ alkyl diphenyl oxide sulphonate.

25. 20. A composition as claimed in Claim 19 in which ingredient D, the detergent active material, is a mixture of mono- and di-C₈₋₁₄ alkyl diphenyl oxide sodium sulphonates.

30. 21. A composition as claimed in any one of Claims 1 to 20 containing about 0.1 to 0.5% of ingredient E, the foam depressant.

22. A composition as claimed in Claim 21 in which ingredient E, the foam depressant, is a mixture of mono- and di-(C₁₆₋₁₈) alkyl acid phosphate esters.

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23. A composition as claimed in any one of Claims 1 to 22 containing about 20 to 30% of ingredient A, the tripolyphosphate.

5. 24. A composition as claimed in Claim 23 in which ingredient A, the tripolyphosphate, is sodium tripolyphosphate.

10. 25. A composition as claimed in any one of Claims 1 to 24 containing about 2 to 5% of ingredient G, the thixotropic thickener, which comprises montmorillonite clay thickener.

15. 26. A composition as claimed in any one of Claims 1 to 24 containing about 2 to 5% of ingredient G, the thixotropic thickener, which comprises attapulgite clay thickener.

20. 27. A composition as claimed in any one of Claims 1 to 26 containing sodium carbonate as ingredient C.

25. 28. A composition as claimed in any one of Claims 1 to 27 having a thixotropy index of about 6 to 8.

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29. A composition as claimed in Claim 1 substantially as specifically described herein with reference to the examples.

5. 30. A method of preparing a composition as claimed in any of the preceding claims comprising first preparing an aqueous dispersion of any ingredient E being employed, mixing the said dispersion with water containing A and B and any C employed, and then mixing the resulting mixture with
10. ingredients D and F and a previously prepared aqueous dispersion of ingredient G.

15. 31. A method of preparing a composition as claimed in any one of Claims 1 to 29 comprising mixing into water, in sequence, ingredient G, half of ingredient A, any E, F, any C, B, the other half of ingredient A, and finally D.

20. 32. A method as claimed in Claim 30 or Claim 31 in which ingredient A has a degree of hydration of less than 1 prior to addition to the composition.

25. 33. A method as claimed in Claim 30, 31 or 32 substantially as specifically described herein with reference to any one of the Examples.

34. A composition whenever made by a method as claimed in Claim 30, 31, 32 or 33.

30.

31.



35. A method of washing dishes in an automatic dishwasher with an aqueous wash bath containing an effective amount of a composition as claimed in any one of Claims 1 to 29 or Claim 34.

5.
