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⑺ Inventor : **Albert, Brigitte**
183 Avenue Joseph Deflandre
B-4053 Embourg (BE)

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⑺ Representative : **Kearney, Kevin David**
Nicholas et al
KILBURN & STRODE 30 John Street
London, WC1N 2DD (GB)

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㉖ Applicant : **Colgate-Palmolive Company**
300 Park Avenue
New York, N.Y. 10022-7499 (US)

⑸ Phosphate-free, gel-like automatic dishwasher detergent compositions.

⑸ Phosphate-free gel-like dishwasher detergent compositions comprising at least one low molecular weight polyacrylate, at least one polymeric thickener, a chlorine bleach compound in an amount to provide 0.2 - 4% available chlorine and water, which is bound to at least one of the other ingredients in the composition. The composition may also contain one or more builder salts, alkali-metal silicate, alkali metal hydroxide, organic detergent, foam depressant and a long chain fatty acid.

The present invention relates to gel-like aqueous liquid automatic dishwasher detergent compositions which are phosphate-free with equivalent cleaning performance and physical stability with improved characteristics as compared to phosphate containing compositions. More specifically, the invention relates to the use of phosphate-free compositions which exhibit excellent cleaning performance and rheological properties.

5 The present invention specifically relates to phosphate-free automatic dishwashing detergent compositions having thixotropic gel-like properties, excellent chemical and physical stability, and which are readily dispersible in the washing medium to provide excellent cleaning performance on 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 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.

15 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 cleaning 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 or 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.

20 The provision of automatic dishwasher compositions in gel form having the afore-described properties has thus far proven problematical, particularly with regard to 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 peptide 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 filming; 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. Thus, U.S. Patent 4,115,308 discloses thixotropic automatic dishwasher pastes containing a suspending agent, e.g. carboxy methyl cellulose (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 C1-(hypochlorite) bleach but no organic surfactant or foam depressant. The product is described, moreover, as a detergent slurry with no apparent thixotropic properties.

30 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.

35 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.

40 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 0.2 to 4% of available chlorine;
- (g) thixotropic thickener in an amount sufficient to provide the composition with thixotropy index of 2.5 to 10;
- (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 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 amounts of nonionic tensides and alkali metal carbonates and/or hydroxides may be used.

The compositions of the instant invention overcome many of the aforementioned deficiencies, while providing compositions which are phosphate-free and consequently environmentally safe.

Quite surprisingly, it was discovered that the phosphate-free compositions of the instant invention while providing compositions which are environmentally safe also provide the desired cleaning performance. They also provided remarkable stabilization against change with time of the rheological properties.

Accordingly, it is an object of the invention to provide liquid ADD compositions having excellent cleaning performance, improved physical stability and improved rheological properties and having a density of 1.20 to 1.44 grams/liter while being phosphate-free and environmentally safe.

It is still another object of the instant invention to provide compositions which have satisfactory chlorine levels with satisfactory stability.

More specifically, it is an object of this invention to provide excellent cleaning performance and improved physical stability of aqueous liquid automatic dishwasher detergent pastes or gels which are phosphate-free.

SUMMARY OF THE INVENTION

These and other objects of the invention, which will become more readily understood from the following summary and detailed description of the invention and preferred embodiments thereof, are achieved by a phosphate-free built aqueous liquid automatic dishwasher detergent composition containing a stabilization system such that when the composition is added to an aqueous wash bath, at a concentration of 10 grams per liter, the wash bath has a pH of at least 11.2.

In accordance with an especially preferred embodiment, the present invention provides a gel-like viscoelastic aqueous automatic dishwasher detergent composition which has a three-dimensional structure and includes, on a weight basis:

- (a) 0 to 20%, preferably up to 20%, eg 1 to 15% of at least one phosphate free detergent builder salt, such as alkali metal carbonate;
- (b) 0 to 20%, preferably up to 20%, eg 1 to 20% of alkali metal silicate;
- (c) 0 to 8%, preferably up to 8%, of alkali metal hydroxide;
- (d) 0 to 5%, preferably up to 5%, of organic detergent active material, which is preferably chlorine bleach stable;
- (e) 0 to 5%, preferably up to 5%, eg 0 to 1.5%, preferably up to 1.5%, of stable foam depressant;
- (f) chlorine bleach compound in an amount to provide 0.2 to 4% of available chlorine;
- (g) 1 to 20% of at least one low molecular weight polyacrylate, which is preferably non-crosslinked;
- (h) 0 to 2%, preferably up to 2%, of a long chain fatty acid or a metal salt thereof, preferably in an amount effective to increase the physical stability of the composition;
- (i) 0 to 8%, preferably up to 8%, of sodium sulfate;

(j) 0.1 to 5%, preferably 0.1 to 2.5% of at least one polymeric thickener, preferably having a molecular weight of at least 500,000;

(k) balance water, wherein the water is bound to the said other ingredients in the said composition. Preferably the water is bound by hydration to the polymeric thickener so that the composition is substantially free of unbound water. The total amount of (b) alkali silicate, (c) alkali metal carbonate and (d) alkali metal hydroxide is preferably such as to provide a pH sufficiently high such that when the composition is diluted in an aqueous wash bath to provide a concentration of 10 grams per liter the pH of the aqueous wash bath becomes at least 11.2. The concentration of the alkali metal builder salt, alkali metal hydroxide and alkali metal hydroxide is preferably less than 25 wt.%, more preferably less than 22 wt.%, and most preferably less than 20 wt.%. Desirably the residual amount of the composition remaining in a poly olefinic container after the poly olefinic container is drained of the composition is less 5 wt.% of the original amount of the composition in the container and more preferably less than 2 wt.%.

The invention also provides a method for cleaning dishware in an automatic dishwashing machine with an aqueous wash bath containing an effective amount of the liquid automatic dishwasher detergent (LADD) composition as described above. According to this aspect of the invention, the LADD composition can be readily poured into the dispensing cup of the automatic dishwashing machine and will be sufficiently viscous to remain securely within the dispensing cup until shear forces are again applied thereto, such as by the water spray from the dishwashing machine.

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. In accordance with the present invention, the types and amounts of the alkaline components which are phosphate-free 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.

GENERAL DESCRIPTION OF THE INVENTION

The viscoelastic gel compositions of the instant invention which have a three dimensional structure can be generally described as follows in Table I :

Table I

<u>Ingredient</u>	<u>Amount (A.I.) Wt %</u>
Sodium Sulfate	0 to 8%
Alkali Metal Silicate	0 to 20%
Foam Depressant	0 to 1.5%
Low Molecular Weight Polyacrylate	1 to 20%
Phosphate-free Builder Salt	1 to 20%
Alkali Metal Hydroxide	0 to 8%
Metal Hypochlorite Solution (13%)	1 to 15%
Fatty Acid or Metal Salt of Fatty Acid	0 to 2%
Polymeric Thickener	0.1 to 2.5%
Water	Balance
Organic Detergent Active Material	0 to 5%

wherein the water of the composition is bound by hydration to the polymeric thickener so that the composition has substantially no free water.

Therefore, in accordance with an especially preferred embodiment of this invention, the high alkalinity is achieved in a phosphate-free, 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 about 0 to 20 weight alkali metal silicate, from 0 to about 8 wt % alkali metal hydroxide, from 1 to 20 wt % phosphate-free builder salt, from about 1 to 8% of at least low molecular weight noncrosslinked polyacrylate, from 0.1 to 5 weight percent polymeric thickener and optionally a metal hypochlorite, a foam depressant, and a detergent active material, wherein the pH of 1 liter of aqueous wash bath containing 10 grams of the composition is at least 11.2.

The alkali metal silicate such as sodium silicate, which provides alkalinity and protection of hard surfaces, such as fine china glaze and pattern, is employed in an amount ranging from 1.0 to 20.0 weight percent, preferably 2.5 to 20 weight percent, in the composition. The sodium silicate is generally added in the form of an aqueous solution, preferably having Na₂O:SiO₂ 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 ingredients, especially NaOH and sodium hypochlorite, are also often added in the form of a preliminary prepared aqueous dispersion or solution.

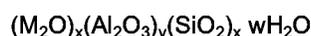
The liquid automatic dishwashing detergent composition contains 1 to 20% by weight of an alkali metal phosphate free detergency builder salt, more preferably 2 to 20% by weight, and most preferably 3 to 20% by weight, wherein the detergency builder is usually an alkali metal carbonate such as sodium carbonate or potassium carbonate.

Other builder salts which can be mixed with the sodium carbonate are gluconates and nitriloacetic eg nitrilotriacetic acid salts. In conjunction with the builder salts are optionally used low molecular weight noncrosslinked polyacrylates having a molecular weight of 1,000 to 100,000, more preferably 2,000 to 80,000. A preferred low molecular weight polyacrylate is Sokalan (Trade Mark) PA30CL manufactured by BASF and having a molecular weight of 8,000. Another preferred low molecular weight sodium salt of a polyacrylate is Norasol LMW45ND which is also known as Acusol 445N manufactured by Norsoshaas and having a molecular weight of 4,500.

Other useful low molecular weight noncrosslinked polymers are: Acusol (Trade Mark) 640D provided by Rohm & Haas; Norasol QR1014 from Norsoshaas having a gel permeation chromatography (GPC) molecular weight of 10,000. Norasol A-1 has a molecular weight of 60,000. Sokalan PA30CL from BASF is the most preferred because of its extremely high bleach stability of at least six months as compared to the other listed low molecular weight polymers which all have bleach stabilities or less than six months. Sokalan PA30CL is a polyacrylate of a chemical structure similar to Norasol LMW45 which has been modified to have increased bleach stability it is believed by the elimination of heavy metals used in the synthesis of the Sokalan PA30CL.

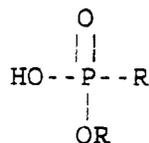
Acusol 445N is an excellent dispersant for calcium carbonate which is formed during the washing process, wherein the Acusol 445N controls crystal growth of the calcium carbonate and helps suspend the calcium carbonate in the wash bath. Another especially useful low molecular weight polyacrylate polymer is Good-Rite (Registered Trade Mark) K-7058N which is a 90 - 100% neutralized sodium salt of a polyacrylate polymer having a molecular weight of 5,800. K-7058N is a good dispersant for calcium carbonate and excellent builder or sequestering agent for heavy metal ions such as calcium or magnesium. A combination of Acusol 445N and K-7058N provides maximum enhancement for the alkali metal non phosphate builder salt such as sodium carbonate. The chlorine stability of a composition made with a combination of Acusol 445 and Good-Rite (Registered Trade Mark) K7058N is employed over compositions made with either Acusol 445 or Good-Rite (Registered Trade Mark) K7058N alone.

Another class of builders useful herein are the water insoluble aluminosilicates, both of the crystalline and amorphous type. Various crystalline zeolites (i.e. aluminosilicates) are described in British Patent No. 1,504,168, U.S. Patent No. 4,409,136 and Canadian Patent Nos. 1,072,835 and 1,087,477. An example of amorphous zeolites useful herein can be found in Belgian Patent No. 835,351. The zeolites generally have the formula:



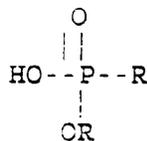
wherein x is 1, y is from 0.8 to 1.2 and preferably 1, z is from 1.5 to 3.5 or higher and preferably 2 to 3 and w is from 0 to 9, preferably 2.5 to 6 and M is preferably sodium. A typical zeolite is type A or similar structure, with type 4A particularly preferred. The preferred aluminosilicates have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

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 the inorganic or organic builder salt 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 phosphoric acid esters of the formula:



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and especially the alkyl acid phosphate esters of the formula:



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15 In the above formulas, one or both R groups in each type of ester may represent independently a C₁₂-C₂₀ alkyl or ethoxylated alkyl group. The ethoxylated derivative 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- C₁₆-C₁₈, alkyl acid or ethoxylated alkyl phosphate esters such as monostearyl/distearyl acid phosphate 1.2/1, and the 3 to 4 mole ethylene oxide condensates thereof. When employed, proportions of 0 to 5 weight percent, preferably 0.1 to 1.5 weight percent, of foam depressant in the composition is typical. 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, sodium stearate, are also effective as foam killers.

Although any chlorine bleach compound may be employed in the composition of this invention, such as dichloroisocyanurate, dichloro-dimethyl hydantoin, or chlorinated trisodium polyphosphate (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 1.5 to about 3.1% 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 (13% of available chlorine) contains or provides roughly the same percentage of available chlorine. 0.8 to 1.6% by weight of available chlorine is especially preferred.

35 Detergent active material which may be useful herein must be stable in the presence of chlorine bleach, especially hypochlorite bleach, and those of the organic anionic, amine oxide, phosphine oxide, sulphoxide or betaine water dispersible surfactant types are preferred; the first mentioned anionics being most preferred. They may be used in amounts ranging from 0 to 5%, preferably 0.1 to 5.0%. 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 (Trade Mark) 3B-2 and DOWFAX (Trade Mark) 2A-1. Alkyl ether sulfates (C₁₂-C₁₄ 3EO-SO₃-Na⁺) are suitable surfactants. 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 alcohol sulphate; sodium C₁₀-C₁₈ alkane-sulphonates 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 sulphoxide RR¹SO can be employed. Betaine surfactants are typically of the structure R₂R¹N←R²COO-, in which each R represents a lower alkylene group having from 1 to 5 carbon atoms, R¹ being as defined above in respect of the amine oxide surfactants. Specific examples of these surfactants include lauryl-dimethylamine oxide, myristyl-dimethylamine oxide, the corresponding phosphine oxides and sulphoxides, and the corresponding betaines, including dodecyl-dimethylammonium acetate, tetradecyl-diethylammonium pentanoate, hexadecyl-dimethylammonium hexanoate and the like. For biodegradability, the alkyl groups in these surfactants should be linear, and such compounds are preferred.

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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.

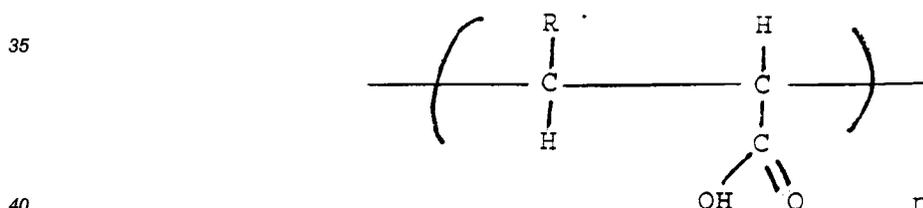
Other useful surfactants are Akypos from Chemy which is a nonionic surfactant terminated by one functional carboxylate; C₁₂₋₃₀ 3EO ether sulfates; and C₁₂₋₁₈ alcohol sulfates.

Thixotropic thickeners, i.e. thickeners for 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. These materials are generally used in amounts of about 0.1 to 4.0 percent by weight, preferably 0.2 to 3.5 weight percent, more preferably 0.3 to 3 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. Those especially preferred generally comprise the inorganic, colloid-forming clays of smectite and/or attapulgite types. 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, attapulgite, 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 polymeric thixotropic thickeners are usually polyacrylate resins such as Carbopol 614 or Carbopol 940 or 624.

Exemplary of the polycarboxylate type thickening agents are cross-linked polyacrylic acid type thickening agents sold by B.F. Goodrich under their Carbopol trademark, including both the 900 series resins, especially Carbopol 941, which is the most ion-insensitive of this class of polymers, and Carbopol 940 and Carbopol 934, and the 600 series resins, especially Carbopol 614. The Carbopol 600 and 900 series resins are hydrophilic high molecular weight, cross-linked linear acrylic acid polymers having an average equivalent weight of 76, and the general structure illustrated by the following formulas:



wherein R can be hydrogen or an alkyl chain. Carbopol 941 has a molecular weight of 1,250,000; Carbopol 940 has a molecular weight of approximately 3,000,000. The Carbopol 900 series resins are highly branched chained and highly cross-linked with polyalkenyl polyether, e.g. 1% of a polyalkyl ether of sucrose having an average of 5.8 allyl groups for each molecule of sucrose. The preparation of this class of cross-linked carboxylic polymers is described in U.S. Patent 2,798,053. Further detailed information on the Carbopol 900 series resins is available from B.F. Goodrich, see, for example, the B.F. Goodrich catalog GC-67, Carbopol® Water Soluble Resins.

In general, these thickening resins are preferably water dispersible copolymers of an alpha-beta monoethylenically unsaturated lower aliphatic carboxylic acid cross-linked with a polyether of a polyol selected from oligo saccharides, reduced derivatives thereof in which the carbonyl group is converted to an alcohol group and pentaerythritol, the hydroxyl groups of the polyol which are modified being etherified with allyl groups, there being preferably at least two such allyl groups per molecule.

These water-dispersible cross-linked thickening resins as described in the aforementioned U.S. Patent 2,798,053 and which have been commercialized by B.F. Goodrich as the Carbopol 900 series resins are prepared from essentially linear copolymers. More recently, B.F. Goodrich has introduced the Carbopol 600 series resin. These are high molecular weight, non-linear moderate branched chain polyacrylic acid cross-linked with

polyalkenyl ether. In addition to the non-linear or branched nature of these resins, they are also believed to be more highly cross-linked than the 900 series resins and have molecular weights between 1,000,000 and 4,000,000.

Most especially useful of the Carbopol 600 series resins are Carbopol 614 and Carbopol 624 which are the most chlorine bleach stable of this class of thickening resins. Carbopol 614 and 624 are also highly stable in the high alkalinity environment of the preferred liquid automatic dishwasher detergent compositions and are also highly stable to any anticipated storage temperature conditions from below freezing to elevated temperatures as high as 120°F (49°C), preferably 140°F (60°C), and especially 160°F (71°C), for periods of as long as several days to several weeks or months or longer.

While the most favorable results have now been achieved with Carbopol 614 moderate branched chain polyacrylic resin, other branched cross-linked polycarboxylate-type thickening agents can also be used in the compositions of this invention. As used herein "polycarboxylate-type" refers to water-soluble carboxyvinyl polymers of alpha, beta monoethylenically unsaturated lower aliphatic carboxylic acids, which may be linear or non-linear, and are exemplified by homopolymers of acrylic acid or methacrylic acid or water-dispersible or water-soluble salts, esters or amides thereof, or water-soluble copolymers of these acids or their salts, esters or amides with each other or with one or more other ethylenically unsaturated monomers, such as, for example, styrene, maleic acid, maleic anhydride, 2-hydroxyethylacrylate, acrylonitrile, vinyl acetate, ethylene, propylene, and the like, and which have molecular weights of from 500,000 to 10,000,000 and are cross-linked or interpolymerized with a multi-vinyl or multi-allylic functionalized cross-linking agent, especially with a polyhydric compound.

These homopolymers or copolymers are characterized by their high molecular weight, in the range of from 500,000 especially from 1,000,000 to 4,000,000, and by their water solubility, generally at least to an extent of up to 5% by weight, or more, in water at 25°C.

The thickening agents are used in their cross-linked form, wherein the cross-linking may be accomplished by means known in the polymer arts, as by irradiation, or, preferably, by the incorporation into the monomer mixture to be polymerized of known chemical cross-linking monomeric agents, typically polyunsaturated (e.g. diethylenically unsaturated) monomers, such as, for example, divinylbenzene, divinylether of diethylene glycol, N,N'-methylenebisacrylamide, polyalkenylpolyethers (such as described above), and the like. Typically, amounts of cross-linking agent to be incorporated in the final polymer may range from 0.01 to 5 percent, preferably from 0.05 to 2 percent, and especially, preferably from 0.1 to 1.5 percent, by weight of cross-linking agent to weight of total polymer. Generally, those skilled in the art will recognize that the degree of cross-linking should be sufficient to impart some coiling of the otherwise generally linear or non-linear polymeric compound while maintaining the cross-linked polymer at least water dispersible and highly water-swallowable in an ionic aqueous medium.

The amount of the high molecular weight, branched chained cross-linked polymeric acid or other high molecular weight, hydrophilic cross-linked polycarboxylate thickening agent to impart the desired rheological property of linear viscoelasticity to the instant compositions will generally be in the range of from 0.1 to 4.0%, based on the weight of the composition, although the amount will depend on the particular cross-linking agent, ionic strength of the composition, hydroxyl donors and the like, wherein mixtures of two or more polymeric thickening agents can be employed.

The bleach stability of the compositions can be improved by employing in the composition a cross-linked linear polyacrylate homopolymer type thickening agent which is substantially formed in non aromatic solvents in place of the Carbopol polymer which are branched chained, crosslinked polyacrylic acid type thickening agents. These crosslinked linear polyacrylate homopolymer type thickening agents are sold by 3-V Chemical corporation under the names Polygel DB (Registered Trade Mark), Polygel DK (Registered Trade Mark) and are manufactured by polymerization in a trichloroethan non aromatic solvent such that they are free of aromatic solvents. The Polygel DB® and Polygel DK® have an Mw of 2,000,000 to 4,000,000.

The amount of the high molecular weight, cross-linked polyacrylic acid or other high molecular weight, hydrophilic cross-linked polyacrylic acid-type thickening agent to impart the desired rheological property of linear viscoelasticity will generally be in the range of from 0.1 to 2%, preferably from 0.2 to 1.4% by weight, based on the weight of the composition, although the amount will depend on the particular cross-linking agent, ionic strength of the composition, hydroxyl donors and the like.

Another class of polymers useful in the instant composition are based on methyl vinyl ether/maleic anhydride copolymers and terpolymers. Examples of useful polymers are: methyl vinyl ether, maleic anhydride, acrylic acid, crosslinked; methyl vinyl ether, maleic anhydride, vinyl pyrrolidone, cross-linked; and methyl vinyl ether, maleic anhydride, isobutene, cross-linked. The cross-linking agent is essential to establish the kind of polymer network useful in this invention. The cross-linking agent can be any hydrocarbon with a chain length of four or more carbon atoms containing at least two carbon-carbon double bonds. The cross-linking agent is

mainly a hydrocarbon with optional halogen and oxygen-containing substituents and linkages such as ester, ether and OH groups. These cross-linking agents can vary in amount from 0.01 to 30% by weight of the total quantity of polymer used. examples of cross-linking agents are 1,7-Octadiene, 1,9 Decadiene, non-terminal dienes, Divinyl Glycol, Butane Divinylether, polyallyl pentaerythritol and polyallyl sucrose. Cross-linking can also be achieved through the maleic anhydride after the polymer is formed, via ester or amide formation using polyols and polyamines such as 1,4 butane diol and polyethylene glycols.

The most useful polymers of these inventions are the Gantrez AN cross-linked with aliphatic dienes such as 1,7 octadiene and 1,9 decadiene.

Gantrez AN polymers cross-linked with from .01 to 10% by weight of 1,7 octadiene were shaken overnight in order to hydrolyse the maleic anhydride ring. The polymer solutions were neutralized to pH 7 to fully ionize the carboxyl groups. The results show that 5% by weight of cross-linking agent is necessary before a gel is formed. If Gantrez AN is cross-linked with 1,9 decadiene then a gel is formed at 3-4% cross-linking.

The cross-linking causes the formation of a polymer that disperses in water to form a gel with a yield point. Table II gives typical yield points for the polymer cross-linked with 1,9 decadiene.

Table II. Yield Point^a as a Function of Polymer Concentration in Water for Cross-linked Gantrez (Gantrez ACV-4006 Cross-linked with 1,9 Decadiene).

Polymer Concentration (Weight %)	PH	Yield Point, Pa
0.125	7	37
0.250	7	64
0.500	7	176

^aMeasurements were made using the Haake Rotoviscometer RV12 with MV IP sensor system. Shear rate was varied from 0 to 10 sec^{-1} .

Brookfield viscosity measurements were made using cross-linked Gantrez polymers, and results are summarized in Table III. Results show that even at very low concentrations, cross-linked Gantrez yield highly viscous polymer solutions.

These viscosities characterize the degree of polymerization of the polymers.

Periodic Table of the Elements can also be used. A key requirement is that the metal salt of the fatty acid must be dispersible in the aqueous medium containing the Carbopol within the composition. The most preferred metal cations are selected from Group IA. 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 and sodium salts are especially highly preferred as generally safe food additives. Sodium stearate is the most preferred species of the instant invention.

The amount of the fatty acid salt stabilizer to achieve the desired enhancement of physical stability and viscosity enhancement 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, other LADD ingredients, as well as the anticipated storage and shipping conditions.

Generally, however, amounts of the metal fatty acid salt or fatty acid stabilizing agents in the range of from 0 to 0.4 wt.%, preferably from 0.005 to 0.6 wt.%, especially preferably from 0.04 to 0.50 wt.%, and most preferably 0.02 to 0.4 wt.%, 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. To obtain the maximum benefit of the fatty acid or the metal salt of the fatty acid it is critical that they must be properly dispersed in the medium containing the polymeric thickener.

Depending on the amounts, proportions and types of physical stabilizers and thixotropic agents, the addition of the fatty acid salt or fatty acid not only increases physical stability, but also provides a simultaneous increase in apparent viscosity. Ratios of fatty acid salt or fatty acid to thixotropic agent in the range of from 0.02-0.4 weight percent fatty acid salt and from 0.1 - 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.

Other conventional ingredients may be included in these compositions in small amounts, generally less than 3 weight percent, such as perfume, preservatives, dyestuffs and pigments and the like, all of course being stable to chlorine bleach compound and high alkalinity (properties of all 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.

DETAILED DESCRIPTION OF THE INVENTION

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

Example 1

The following compositions, Examples 1A to 10, were formulated and their compositions are given in Tables 1A to 1C.

Example 1 (contd.)

Table 1B

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	F	G	H	I	J
Anhydrous Sodium Sulfate	0.0	0.0	0.0	0.0	0.0
13% Sodium Hypochlorite Solution (13% available chlorine)	1.3	1.3	1.3	1.3	1.3
Sodium/disilicate	17.2	17.2	13.7	13.7	17.2
Didecyldiphenyl ether disulfonate	0.46	0.46	0.46	0.46	0.46
Ethoxamer Monodi Phosphate Ether	-	-	-	-	-
Stearic Acid	0.25	0.15	0.15	0.15	0.15
Potassium Carbonate	-	-	8.0	-	-
Anhydrous Sodium Carbonate	4.0	4.0	2.0	10.0	4.0
Na ₂ O Caustic soda (38%)	3.28	3.28	3.42	3.42	3.42
Carbopol 614	0.5	0.5	0.75	0.75	0.75
Norasol LMW-45NX (polyacrylic builder dispersion in water at 45% concentration)	3.6	3.6	4.5	4.5	-
Softened Water	← ----- Balance ----- →				4.5
Sokalan PA 30CL					
Norasol LMW-45NX					
Norasol QR1014					
Norasol A-1					
Serdet DCK 30 C ₁₂ -C ₁₄ 3EO SO ₃ -Na+					
SLS C ₁₂ -C ₁₄ 3EO SO ₃ -Na+					
Aktype MB 2621					

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Example 1 (contd.)

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Table 1C

	<u>K</u>	<u>L</u>	<u>M</u>	<u>N</u>	<u>O</u>
Anhydrous Sodium Sulfate	0.0	0.0	0.0	0.0	0.0
13% Sodium Hypochlorite Solution (13% available chlorine)	1.3	1.3	1.3	1.3	1.3
Sodium/disilicate	17.2	17.2	17.2	17.2	17.2
Didacyldiphenyl ether disulfonate	0.46	0.46	-	-	-
Ethoxamer Monodi Phosphate Ether					
Stearic Acid	0.15	0.15	0.15	0.15	0.15
Potassium Carbonate					
Anhydrous Sodium Carbonate	4.0	4.0	4.0	4.0	4.0
Na ₂ O Caustic soda (38%)	3.42	3.42	3.42	3.42	3.42
Carbopol 614	0.75	0.75	0.75	0.75	0.75
Norasol LMW-45NX (polyacrylic builder dispersion in water at 45% concentration)					
Softened Water	← ----- Balance ----- →				
Sokalan PA 30CL					
Norasol LMW-45NX	0.0		4.5	4.5	4.5
Norasol QR1014	4.5				
Norasol A-1		4.5			
Serdet DCK 30 C ₁₂ -C ₁₄ 3EO SO ₃ -Na+			0.46		
SLS C ₁₂ -C ₁₄ 3EO SO ₃ -Na+				0.46	
Akypo MB 2621					0.46

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The procedure for forming the formulations of Examples 1A to 10 comprises forming a first aqueous solution A' by adding at room temperature under mixing conditions first the dispersion of the Norasol LMW-45NX into the water, secondly, the Carbopol 614 and thirdly, a sufficient amount of caustic soda to just neutralize the polycarboxylate polymer. A second aqueous solution (B') is formed by adding at room temperature under conditions of mixing to the water, first the builder salt, secondly, the sodium sulfate, thirdly, the sodium disilicate and lastly, the balance of the caustic soda. A third aqueous solution (C') which is entitled the premix is formed at 60-70°C by adding to water (3 parts) first the dodecyldiphenyl ether disulfonate (0.46 parts) and secondly, the stearic acid (0.15 parts). Solution B' is added under conditions of mixing at room temperature to Solution A'. The mixed solutions of A' & B' at room temperature under conditions of mixing is added the third solution (C'). The combined solutions of A', B' and C' the 13% hypochlorite solution to form the final formulations of Examples 1A to 10.

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Example 2

Formulations 1A-10 were tested for soil removal on dishes in a standard multi-soil test using a Bosch SMS521 (dishwasher) at 65°C wherein 3 ml. of Galaxy rinse aid sold by Colgate Palmolive Co. was used. A rating system of 1-10 was used with 10 representing maximum soil removal and the results are given in Table 2 below.

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Table 2

	<u>Example</u>	<u>Porridge (cutlery & plates)</u>	<u>Rice (dishes & cutlery)</u>	<u>White Sauce (dishes)</u>
5				
10	1A	8.0	8.5	9.25
	1B	8.1	9.25	8.8
	1C	7.4	7.5	8.25
15	1D		6.6	8.25
	1E			
	1F			
20	1G			
	1H			
	1I	6.8	7.25	9.25
	1J			
25	1K	7.6	6.5	8.5
	1L	7.4	6.6	7.2
	1M			
30	1N			
	1O			
	Galaxy	6.2	7.5	8.8

35 MULTI-SOIL TEST

This method allows one to evaluate the removal of critical soils on several representative items of dishes as well the performance on soiled glasses.

40 METHODOLOGY:

- . Dishwasher : Bosch SMS 5021
- . Recommended Dosage: 55 g
- . Dishwasher Load:

45 Lower Basket :

- . 6 Plates with Porridge Soils
- . A Stainless Steel Plate with Rice Soils
- . A Stainless Steel Plate with White Sauce
(mixture made fom milk, flour, butter)
- . Cutleries in the Cutlery Basket:
with Rice (2 spoons, 2 knives), 2 forks)
with Porridge (2 spoons + 2 knives)

50

Upper Basket:

- . 8 Glasses Soiled with Tomato Juice
- . 8 Glasses Soiled with Cocoa Beverage
- . 8 Glasses Soiled with Milk

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4 products are tested simultaneously in 4 dishwashers according to the statistical procedure made in "Latin Square". A wash cycle with 4 replicates per product.

EP 0 519 603 A1

. pH value is measured during wash cycle

. Washing Program:

. Prewash

. Main Wash at 65° C

. Rinse Cycle

. Drying

Water hardness during wash: 100-150 ppm CaCO₃.

. EVALUATION:

. Each piece of dishes is evaluated according to a scale from 0 (no removal) to 10 (complete soil removal).

. The glasses are evaluated in a viewing box in

. overall performance (from 0 to 10)

. per item of performance as

. Filming (on a scale from 0 to 4 (no filming)

. Spotting (0 to 4 (no spotting)

. Soil Redeposition (0 to 4)

Example of results shown in the preceding Table.

The results are shown in Tables 3A to 3C below.

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Table 3A

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
<u>RHEOLOGICAL DATA AT RT</u>					
1. G' (Pa) ²	57	56	21		
G'' (Pa)	24	27	13		Very Thick
2. M (Pa.S) ³	1.5	-	1.6		
<u>APPEARANCE</u>	-----Translucent-----				
<u>CHLORINE STABILITY AT RT</u>	61%	59%	63%	72%	
(% remaining chlorine after 3 months ageing)					
<u>PHYSICAL STABILITY</u>	OK	OK	OK ⁴	OK	OK
at RT after 3 month ageing (presence of syneresis)			phase separation		

Notes on Table 3

¹ As measured on CARRIMED Model CSL (Cell: cone-plate-gap: 53 micrometers - cone angle: 4 degrees - cone diameter: 2cm) operating in oscillating mode under "structure recovery" experiment (recorded 11 84 sec. after structure destroying - frequency: 1 Hz - torque: 100 M N. m. Tested after one month.

² Recorded on Rheomat 108 at 17.7 sec⁻¹. Tested after two weeks.

³ Presence of phase separation at 35°C after 1 month ageing.

⁴ For stearic acid dispersion.

Table 3B

	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>	<u>J</u>
5	<u>RHEOLOGICAL DATA AT RT</u>				
	G' (Pa) ²	13	3	56	25
	G" (Pa)	8.5	4.5	27	15
10	M (Pa.S) ³	1.4	0.9		

15	<u>APPEARANCE</u>	-Translucent-	White
			Trans-
			lucency

20	<u>CHLORINE STABILITY AT RT</u>	59%	52%	75%
	(remaining chlorine after month ageing)			

25	<u>PHYSICAL STABILITY</u>	OK	OK	OK	OK	OK
	(RT after 3 month aging presence of syneresis)					

30 The appearance of J is translucent.

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Table 3C

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K L M N O

RHEOLOGICAL DATA AT RT

10

G' (Pa)²

15 10

G'' (Pa)

12 13 OK OK OK

15

M (Pa.s)³

APPEARANCE

-----Translucent-----

20

CHLORINE STABILITY AT RT

78% 77%

(remaining chlorine after
month ageing)

25

PHYSICAL STABILITY

OK OK⁴

(RT after 3 month ageing
presence of syneresis)

phase
separation

30

RHEOLOGICAL DETERMINATION

CARRIMED (model: CSL 100):

35

This apparatus is equipped to operate in oscillating mode in order to fully assess the viscoelastic behavior of Carbopol-based No P gels. This method is attractive for its "in depth" characterization of gel structures because several experiments can be carried out to test completely one sample.

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One experiment usually done on gels is "The Structure Recovery": This one allows to characterize how the gel structure is recovered after breakage by an high steady stress:

STRUCTURE RECOVERY MEASURING CONDITIONS:

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. The samples are studied first after 1 week aging (i.e. when the structure is obtained) and on aging. (1 month, 2 months, 3 months) at different storage temperatures.

The Carbopol NOP Gels are observed to be rheologically stabilized within 2 weeks - 1 month period.

. Cell for measuring: Cone-Plate (gap: 53 Mm - cone angle: 4 degrees - (cone diameter: 2 cm)

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. The gel structure is broken, first by a steady stress of 400N/m² during 1'. After an equilibrium time of 10 sec, storage modulus (G') representative of the elastic component and loss modulus (G'') representative of the viscous component are determined versus recovery time. In oscillating mode:

Measuring Conditions:

Torque: 100 micro N.m

Oscillation Frequency: 1 Hz

Thermostatisation Temp.: 20° C

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The moduli are observed to be stabilized around 20' (minutes) (1200 sec).

RHEOMAT 30 (CONTRAVES):

This apparatus observes the rotational viscometer principle operating in steady mode to determine the apparent viscosities on a large range of shear rates (30-32 values).

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PRINCIPLE:

The concentric measuring cell is based on a measuring head and measuring tube rigidly coupled together, the measuring bob being driven by a DC motor. The braking torque exerted by the sample results in a change in the motor's armature current. Translated in viscosity, shear stress and shear rate from measuring conditions. The data are then analyzed in terms of

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Casson Law

$$(\sqrt{G} \text{ (Pa)}) = \sqrt{G_o} + \eta\sqrt{\gamma}$$

15

or
Bingham Law

$$(G = G_o + \eta\gamma)$$

G = shear stress γ = shear rate gradient η = Viscosity G_o = initial shear stress.

(Type of cell: Setting B)

Measurement Temp.: 25°C).

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RHEOMAT 108 (CONTRAVES):

Uses the same principle as Rheomat 30. But only operates at selected shear rate appropriate to conditions and tested sample.

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Viscosity measurement is done after perturbation 30 sec.

SETTING FOR CARBOPOL-BASED FORMULAE:

Cell: 2 Rate: 1 ($\gamma = 17.7 \text{ sec}^{-1}$)

(Minimum value detectable: 0.8 Po sec)

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PHYSICAL STABILITY.

The samples are stored in small glasswares (brown to avoid UV influence) and the physical stability is visually determined on aging at 3 temperatures of storage 4°C, 35°C, RT.

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The sample is considered as physically stable when no presence of syneresis is observed on ageing (syneresis: liquid separation from gel in bottom of glassware.)

Example 3

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Formulas 3A-3J were formulated according to the following procedure. A-E are given in Tables 4A and F-J in Table 4B.

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Table 4A

5 Example 3A 3B 3C 3D 3E

10	Carbopoi 614	1.0	1.0	0	0	0
	Polygel DK	0	0	1.0	1.2	0
15	Gantrez (13%)	0	0	0	0	21.34
20	Sodium Selite (47.5%)	25.0	25.0	25.0	25.0	25.0
25	NaOH (50%)	4.5	4.5	4.5	4.5	7.0
30	Good-Rite K- 7058N(45%)	18.5	7.75	7.75	7.75	13.9
35	Acusol 445N (45%)	0	7.75	7.75	7.75	--
40	Sodium Carbonate	6.0	6.0	6.0	0	0
45	Sodium Fluoride	0	0	0	0	0
50	Dowfax 3B2 (45%)	0.8	0.8	0.8	0.8	0.8

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Table 4A (contd.)

5	Fatty Acid ¹	0.1	0.1	0.1	0.1	0
	NaOCl (12%)	9.2	10.0	12.0	12.0	10.0
10	Colorant	.003	.003	.003	.003	.003
	Fragrance	.03	.03	.03	.03	.03
15	Sodium Stearate	0	0	0	0	0.1
	Water	Balance	Balance	Balance	Balance	Balance
20	A/2 ⁰³ / Sodium Benzoate					
25	Density	1.28	1.27	1.26	1.27	1.22
30	Spotting ²	1.6	1.25	1.20	-	1.0
	Filming ³	3.0	2.1	2.1	-	3.0
35	Viscosity ⁴	6750	3700	4700	5750	3400
40	C1 Avg [‡]	0.99	1.01	1.33	1.10	1.05

Notes on Table 4A

45 ¹Fatty acid is a mixture of stearic acid and palmitic acid -
ratio 1:1

50 ²Tested according to ASTM D-3566-79

³Tested according to ASTM 2-3566-79

55 ⁴Brookfield HATD Model Spindle #4 20 rpms, R.T. reading taken
after 90 seconds of shear on example.

Example 3 (contd.)

Formulas 3F-3J were formulated according to the following procedure.

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Table 4B

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Examples 3F 3G 3H 3I 3J

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Carbopoi 614	1.0	1.0	1.0	1.0	1.0
Polygel DK	0	0	0	0	0
Gantrez (13%)	0	0	0	0	0
Sodium Selicate (47.5%)	25.0	25.0	25.0	25.0	25.0
NaOH (50%)	4.5	4.5	4.5	4.5	4.5
Good-Rite K- 7058N(45%)	9.25	7.75	7.75	7.75	7.75
Acusol 445N (45%)	9.25	7.75	7.75	7.75	7.75
Sodium Carbonate	0	5	5	5	5
Sodium Fluoride	0	6	6	0	6
Dowrax 3B2 (45%)	0.8	0.8	0.8	0.8	0.8

Table 4B (contd.)

5	Fatty Acid ¹	0	0.1	--	0.1	
	NaOCl (12%)	10.0	9.2	9.2	10.0	9.2
10	Colorant	.003	.003	.003	.003	.003
	Fragrance	.03	.03	.03	.03	.03
15	Sodium Stearate	0.1	0	0.1	0	0.1
20	Water	Balance	Balance	Balance	Balance	Balance
	A/2 ⁰³ / Sodium Benzoate				/1.5	1.0/
25	Density	1.23	1.32	1.32		1.33
30	Spotting ²	1.0	1	2		2
	Filming ³	2.6	2.0	2		4
35	Viscosity ⁴	2800	3980	3620	6500	4690
40	Cl Avg ⁵	1.04	0.93	0.94	1.05	0.93

¹Fatty acid is a mixture of stearic acid and palmitic acid -
ratio 1:1

²Tested according to ASTM D-3566-79

³Tested according to ASTM 2-3566-79

⁴Brookfield HATD Model Spindle #4 20 rpms, R.T. reading taken
after 90 seconds of shear on sample.

⁵The above formulas were made by first making an aqueous solution of the cross-linked polymer such as Carbopol 614 at room temperature and subsequently neutralizing the polymer under mild agitation at room temperature first with the sodium silicate and then the sodium hydroxide. The 7058 polymer was then added with stirring followed by the 44 SN polymer. To the resultant solution was added with stirring the sodium carbonate

then an aqueous solution of the NaF (if present), then an emulsion of the Dowfax 3B2 and the fatty acid or sodium stearate, then the bleach was added with stirring and finally the fragrance was added with stirring if A/203 or sodium benzoate were added, they were post added to the composition with stirring.

5 The emulsion of the Dowfax 3B2 and fatty acid or sodium stearate was formed by first heating the Dowfax 3B2 to a temperature of 70-80°C and the powdered fatty acid or sodium stearate was added to the heated Dowfax 3B2 with stirring. The formed heated emulsion was then added to the batch.

Claims

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1. An aqueous automatic dishwasher composition comprising by weight:

- (a) 0 to 20% of at least one phosphate free builder salt;
- (b) 0 to 20% alkali-metal silicate;
- (c) 0 to 8% alkali metal hydroxide;
- 15 (d) 0 to 5% organic detergent active material;
- (e) 0 to 5% foam depressant;
- (f) chlorine bleach compound in an amount to provide 0.2 to 4% of available chlorine;
- (g) 1 to 20% of at least one low molecular weight polyacrylate;
- (h) 0 to 2.0% of a long chain fatty acid or a metal salt thereof;
- 20 (i) 0 to 8% sodium sulfate;
- (j) 0.1 to 2.5% of at least one polymeric thickener; and
- (k) water, wherein the said water is bound to at least one of the said other ingredients in the said composition.

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2. A composition as claimed in Claim 1 characterised in that the polymeric thickener has a molecular weight of at least 500,000.

3. A composition as claimed in Claim 1 or Claim 2 characterised in that the water is bound by hydration to the polymeric thickener so that the composition is substantially free of unbound water.

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4. A composition as claimed in Claim 1, 2 or 3 characterised in that the detergent builder salt is sodium carbonate.

5. A composition as claimed in any one of Claims 1 to 4 characterised in that the foam depressant is in the range of from 0.1 to 1.5%.

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6. A composition as claimed in any one of Claims 1 to 5 characterised in that the detergent active material is in the range of 0.1 to 5.0%.

7. A composition as claimed in any one of Claims 1 to 6 characterised in that the chlorine bleach compound is sodium hypochlorite.

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8. A composition as claimed in any one of Claims 1 to 7 characterised in that the foam depressant is an alkyl acid phosphate ester, an alkyl phosphoric acid ester containing one or two C₁₂₋₂₀ alkyl or ethoxylated alkyl groups.

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9. A composition as claimed in any one of Claims 1 to 8 characterised in that the amount of components is such that when the composition is diluted to 10 g/l the pH of the diluted composition is from 11.2 to 13.5.

10. A composition as claimed in any one of Claims 1 to 9 characterised in that the concentration of said fatty acid is .005 to 2.0 wt.%.

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11. 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 10 in an amount sufficient to provide a pH of the washbath of at least 11.2.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 4513

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 407 187 (UNILEVER)	1-3, 7, 9, 11	C11D3/395 C11D3/37
A	* page 5, line 21 - line 52; claims 1,8-10,14; example 8 *	4, 6	

A	EP-A-0 373 864 (PROCTER & GAMBLE) * claims; examples *	1-4, 6-9	

A	US-A-4 878 951 (G. POCHARD ET AL.) * claims 1-3,5,7; table 3 *	1-3, 5-8	

A	FR-A-2 620 727 (COLGATE-PALMOLIVE) * claims 11,16,19,20 *	1, 3-10	

			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 AUGUST 1992	Examiner GRITTERN A. G.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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