⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 523 826 A1**

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **92303608.1**

㉒ Date of filing: **22.04.92**

(51) Int. Cl.^{5}: **C11D 17/00**, C11D 3/37, C11D 3/20

㉚ Priority: **11.07.91 US 728150**

㊸ Date of publication of application:
20.01.93 Bulletin 93/03

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IT LI LU NL SE

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(54) Viscoelastic aqueous liquid detergent composition, especially for automatic dishwashers of improved dispensability.

(57) A linear viscoelastic aqueous liquid automatic dishwasher detergent composition comprising water from 0 to about 5% of a compound having the formula R_1COOX wherein x is selected from the group consisting of hydrogen and an alkali metal cation and R_1 is selected from the group consisting of phenyl groups and substitute phenyl groups, from 0 to 5% by weight of a chlorine bleach stable, water dispersible or soluble organic detergent, from 5 to 40% by weight of at least one alkali metal tripolyphosphate, up to 20% by weight of a chlorine bleach compound, and 1.2 to 2.0 weight percent of at least one branched crosslinked polycarboxylate-type thickening agent having a molecular weight of at least 1,000,000.

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BACKGROUND OF THE INVENTION

Liquid automatic dishwasher detergent compositions, both aqueous and nonaqueous, have recently received much attention, and the aqueous products have achieved commercial popularity.

The acceptance and popularity of the liquid formulations as compared to the more conventional powder products stems from the convenience and performance of the liquid products. However, even the best of the currently available liquid formulations still suffer from three major problems, dispensability from the bottle containing the formulations, product phase instability and bottle residue, and to some extent cup leakage from the dispenser cup of the automatic dishwashing machine.

Representative patent art in this area includes Rek, U.S. Patent 4,556,504; Bush, et al., U.S. Patent 4,226,736; Ulrich, U.S. Patent 4,431,559; Sabatelli, U.S. Patent 4,147,650; Paucot, U.S. Patent 4,079,015; Leikhem, U.S. Patent 4,116,849; Milora, U.S. Patent 4,521,332; Jones, U.S. Patent 4,597,889; Heile, U.S. Patent 4,512,908; Laitem, U.S. Patent 4,753,748; Sabatelli, U.S. Patent 3,579,455; Hynam, U.S. Patent 3,684,722. Other patents relating to thickened aqueous detergent compositions include U.S. Patent 3,985,668; U.K. Patent Application GB 2,116,199A; U.S. Patent 4,511,487; U.S. Patent 4,752,409 (Drapier, et al.); U.S. Patent 4,801,395 (Drapier, et al.); U.S. Patent 4,836,946 (Dixit); U.S. Patent 4,889,653 (Ahmed, et al.). Commonly assigned co-pending patents include, for example, Serial No. 427,912 filed October 24, 1989; Serial No. 924,385, filed October 29, 1986; Serial No. 323,138, filed March 13, 1989; Serial No. 328,716, filed March 27, 1989; Serial No 323,137, filed March 13, 1989; Serial No. 323,134, filed March 13, 1989.

The solubilizing effect of potassium salts on sodium tripolyphosphate in aqueous detergent compositions is described in U.S. Patent 3,720,621 (Smeets). U.S. Patent 4,836,948 discloses a viscoelastic gel detergent composition characterized by its viscosity under low and high shear conditions, pH, and steady state viscoelastic deformation compliance. The composition requires the presence of a polycarboxylate polymeric thickener, preferably a crosslinked polyacrylic acid. The compositions of this patent also, however, require a trivalent metal containing material, especially an aluminum containing material such as alumina and may further include a structuring chelant which may be a salt of carbonate, pyrophosphate or mixture thereof, and preferably the potassium salts. The recently issued U.S. Patent 4,859,358 discloses the incorporation of metal salts of long chain hydroxy fatty acids, as anti-tarnishing agents, in thickened aqueous automatic dishwashing detergent compositions. The compositions are not described as being linear viscoelastic and as exemplified do not include any potassium salts. Additionally, this patent claims that the hydroxy fatty acid does not have an effect upon the viscosity of the composition.

Summary of the Invention

According to the present invention there is provided an improved aqueous liquid automatic dishwasher detergent composition. The composition is characterized not only by its linear viscoelastic behavior, substantially indefinite stability against phase separation or settling of dissolved or suspended particles under high and low temperature conditions, very low levels of bottle residue, relatively high bulk density, and substantial absence of loosely bound water, but also by its overall product consistency from batch to batch and run to run and over a wide range of storage and aging conditions, including superior aesthetics, freedom from fish-eyes, absence of crystal formation and growth, and resistance to cup leakage of less than about 10 wt% as well as improved optical properties; and ease of dispensability from the container in which it is stored wherein the composition contains substantially no free (unbound) water.

The present invention was accomplished upon the discovery that an improved automatic dishwashing composition having low foam properties and reduced spotting of glassware can be formulated by employing a crosslinked polyacrylic acid thickening agent at a minimum critical concentration of 1.2 weight percent without the need of employing a fatty acid in the composition to obtain a composition which has linear viscoelastic characteristics.

In the prior art compositions, it has been claimed that a crosslinked polyacrylate thickener and fatty acids/salts are essential to obtain a viscoelastic gel. However, compositions stabilized using fatty acids have several shortcomings. These include:

1. Fatty acids/salts foam severely in soft water. This reduces the mechanical energy input of the dishwasher to the cleaning.
2. Fatty acid salts adversely influence the spotting on glassware.
3. Stringent process requirements (e.g. temperatures, emulsification, etc.) are mandatory for incorporating the fatty acids. Otherwise, products with expected physical properties cannot be obtained.
4. Consistency of the product may change upon aging the product. This in turn influences the flow

properties of the system.

Accordingly, the main objective of the present invention is to develop a stable gel composition, which is free from aforementioned problems, wherein the composition is free from any fatty acid moiety.

The instant invention described herein is based on a space filling model, i.e. the hydynamic phase volume of the polyacrylate gel particles is sufficiently high enough to generate a three dimensional network having viscoelastic properties. The minimum concentration of the crosslinked polyacrylic polymer to achieve such a state is about 1.2% and this concentration window can be varied depending upon the total composition.

Accordingly, in one aspect the present invention provides an improved linear viscoelastic aqueous liquid automatic dishwasher detergent composition comprising substantially bound water, optionally, from 0 to 3% by weight of low-foaming chlorine bleach stable water dispersible or soluble organic detergent, active material, from 10 to 35% by weight of a detergent builder salt, from 3 to 20% by weight of a chlorine bleach compound, from 1.2 to 2.0% of at least one branched chained crosslinked polymeric thickening agent having a molecular weight of at least 1,000,000 optionally from 0 to 5.0% of an organic compound having a carboxylic acid group affixed to a phenyl ring or its salts thereof, and optionally a linear crosslinked polycarboxylate having a molecular weight of 150,000 to 300,000 wherein the compositions preferably have a bulk density of from 1.26 g/cm^3 to 1.42 g/cm^3.

In a preferred embodiment, the linear viscoelastic aqueous liquid automatic dishwasher detergent comprises, by weight,

(a) 10 to 35% detergent builder salt,
(b) 5 to 25% alkali metal silicate;
(c) 0 to 3% chlorine bleach stable, water-dispersible or water soluble organic detergent active material;
(d) 0 to 1.5% chlorine bleach stable foam depressant;
(e) chlorine bleach compound in an amount significant to provide 0.2 to 4% of available chlorine;
(f) 1.2 to 2.0% of at least one branched chained hydrophilic crosslinked water insoluble polycarboxylate thickening agent having a molecular weight of from 1,000,000 to 4,000,000 to provide said linear viscoelastic property;
(g) 0 to 5% of a linear noncrosslinked polyacrylate polymer having a molecular weight of 150,000 to 300,000;
(h) 0 to 5 of an organic compound having the formula R^1COOX wherein X represents a hydrogen atom or an alkali metal cation and R^1 represents a phenyl group or a substituted phenyl group;
(i) 0 to 10% of a non-crosslinked polyacrylic acid having a molecular weight in the range of from 150,000 to 300,000; and
(j) water;

wherein the entire composition has a cup leakage of less than 10 wt%, more preferably less than 8 wt% and most preferably less than 6 wt%; a density of 1.26 to 1.42 g/cc^3, more preferably about 1.32 to 1.42 g/cc^3, and a dispensability of at least 225 grams/minute through a 0.375 inches (8.45 mms) opening under standard gravitational force, when the dispensing bottle is aligned parallel to a vertical axis with the 0.375 inch (8.45 mms) opening oriented towards the ground.

In another aspect of the invention, a method for preparing the aqueous linear viscoelastic composition is provided. According to this aspect, the method comprises the steps of:

I.
  (a) fully hydrating at least one branched chained crosslinked polycarboxylate thickener by slowly adding the thickener to heated water while moderately agitating the mixture;
  (b) slowly adding a neutralizing amount of caustic soda to the mixture from (a) while continuing agitation to obtain a dispersion of the neutralized thickener;
II.
  (c) forming an aqueous mixture of surface active agents which include the surfactant and foam depressant agent;
  (d) heating the mixture in (c) to a temperature higher than that of the heated water in (a) and mixing until a homogeneous smooth premix is obtained;
III.
  (e) uniformly mixing metal builder salt with the dispersion (b);
  (f) uniformly mixing the heated premix (d) with the mixture (e);
  (g) cooling the mixture (f) to a temperature above the temperature of the heated water in step (a);
  (h) adding bleach to the mixture (g);
  (i) adding fragrance to the mixture (h);
  (j) adding the organic compound having a carboxylic acid group affixed to a phenyl ring or a salt

thereof to the mixture (i); and

(k) adding the noncrosslinked polyacrylate polymer to the mixture (i).

In a preferred embodiment of the invention process, the pH of the aqueous slurry of the branched chained crosslinked polycarboxylate thickener after the neutralization in step (b) and in each succeeding step is maintained at a value of at least 11.

Detailed Description and Preferred Embodiments

The compositions of this invention are thickened aqueous liquids containing various cleansing active ingredients, detergent builder salts and other detergent adjuvants, structuring and thickening agents and stabilizing components, although some ingredients may serve more than one of these functions.

The advantageous characteristics of the compositions of this invention, include improved dispensability from its storage container by having a minimum flow rate of 225 grams/minute dispensed through a 0.375" (8.45 mms) opening under normal gravitational force, wherein the preferred flow rate is 225 grams/minute to 325 grams/minute, improved optical properties, improved flow properties upon aging, reduced foaming, reduced spotting of glassware, physical stability, as manifested by little or no phase separation, solid settling or viscosity changes over time or resulting from exposure to low or high temperatures, low bottle residue, low cup leakage of less than 10 wt%, high cleaning performance, e.g. low spotting and filming, soil residue removal, and consistency in product characteristics and performance, and superior aesthetics. These characteristics are believed to be attributable to several interrelated factors such as low solids, i.e. undissolved particulate content, product density and linear viscoelastic rheology. These factors are, in turn, dependent on several critical compositional components and processing conditions of the formulations, namely, (1) the inclusion of at least 1.2 wt. % of at least one salt stable branched chained crosslinked polymeric thickening agent and water exemplified by highly branched chained crosslinked polyacrylic acids, (2) a product bulk density of at least 1.28 g/cc, especially at least 1.32 g/cc, (3) hydrating crosslinked polymeric thickener with heated water, (4) maintaining the pH of the neutralized polymeric thickener at a pH of at least 11, more preferably at least 11.5, and (5) the inclusion in the formula of an organic compound characterized by the formula R^1COOX wherein x represents a hydrogen atom or an alkali metal ion and R^1 represents a phenyl group or a substituted phenyl group, wherein especially preferred organic compounds are benzoic acid or sodium benzoate.

In particular, the linear viscoelastic aqueous liquid automatic dishwasher detergent compositions of this invention will, at least in the preferred embodiments, satisfy each of the following stability criteria over the aging temperature-time schedule shown by the following Table A:

TABLE A

Aging Temperature		Duration (Weeks)	
(°F)	(°C)	Minimum	Preferred
140	60	> 1	> 2
120	49	> 6	> 8
100	38	> 13	> 16
Ambient		> 24	>> 24

More specifically, the compositions are considered stable if each of the following stability criteria is satisfied for at least the minimum number of weeks for each aging temperature shown in Table A:

. no visible phase separation (i.e. no solid/liquid separation)

. no significant change (e.g. less than 10%) in viscosities, yield stress or other dynamic-mechanical properties

. no crystal growth under repeated heating-cooling cycles over a temperature range of at least 70°F to 140°F (21 to 60°C)

. no decolorization or significant color change. In addition to the above stability criteria, the compositions of this invention are further characterized by their ease of dispensability of the formulation from its storage container as manifested by the formulation having a flow rate at room temperature through a 0.375" (8.45 mms) opening of 225 to 325 grams/minutes, wherein the container is aligned parallel to a vertical axis and the opening is oriented towards the ground and the test is done under normal gravitational force. The compositions of the instant invention also exhibit low bottle residue and cup leakage of less than 10 wt%, more preferably less than 8 wt% and most preferably less than 6 wt%. Specifically, for the preferred crosslinked acid thickened compositions of this invention, bottle residues, under the usual use conditions, will be no more than about 6 to 8%, more preferably no more than 4 to 5%, of the original bottle contents, on a weight basis.

At least one of the polymeric thickening agents contributes to the linear viscoelastic rheology of the invention compositions. As used herein, "linear viscoelastic: or "linear viscoelasticity" means that the elastic (storage) modulus (G') and the viscous (loss) modulus (G'') are both substantially independent of strain, at least in an applied strain range of from 0-50%, and preferably over an applied strain range of from 0 to 80%. More specifically, a composition is considered to be linear viscoelastic for the purposes of this invention, if over the strain range of 0-50% the elastic module G' has a minimum value of 100 dynes/sq.cm., preferably at least 250 dynes/sq.cm., and varies less than 500 dynes/sq.cm., preferably less than 300 dynes/sq.cm., especially preferably less than 100 dynes/sq.cm. Preferably, the minimum value of G' and maximum variation of G' applies over the strain range of 0 to 80%. Typically, the variation in loss modulus G'' will be less than that of G'. As a further characteristic of the preferred linear viscoelastic compositions the ratio of G''/G' (tan δ) is less than 1, preferably less than 0.8, but more than 0.05, preferably more than 0.2, at least over the strain range of 0 to 50%, and preferably over the strain range of 0 to 80%. It should be noted in this regard that % strain is shear strain x100.

By way of further explanation, the elastic (storage) modulus G' is a measure of the energy stored and retrieved when a strain is applied to the composition while viscous (loss) modulus G'' is a measure of the amount of energy dissipated as heat when strain is applied. Therefore, a value of tan δ,

$0.05 < \tan \delta < 1$,

preferably

$0.2 < \tan \delta < 0.8$

means that the compositions will retain sufficient energy, when a stress or strain is applied, at least over the extent expected to be encountered for products of this type, for example, when poured from or shaken in the bottle, or stored in the dishwasher detergent dispenser cup of an automatic dishwashing machine, to return to its previous condition when the stress or strain is removed. The compositions with tan δ values in these ranges, therefore, will also have a high cohesive property, namely, when a shear or strain is applied to a portion of the composition to cause it to flow, the surrounding portions will follow. As a result of this cohesiveness of the linear viscoelastic characteristic, the compositions will readily flow uniformly and homogeneously from a bottle at a flow rate of at least 225 grams/minute through a 0.375 inch (8.45 mms) opening when the bottle is tilted parallel to a vertical axis, thereby contributing to the physical (phase) stability of the formulation and the low bottle residue (low product loss in the bottle) which characterizes the invention compositions. The linear viscoelastic property also contributes to improved physical stability against phase separation of any undissolved suspended particles by providing a resistance to movement of the particles due to the strain exerted by a particle on the surrounding fluid medium. Linear viscoelasticity also contributes to the elimination of dripping of the contents when the product is poured from a bottle and hence reduction of formation of drops around the container mouth at the conclusion of pouring the product from a container.

A still further attribute of the invention compositions contributing to the overall product stability and low bottle residue is the high water absorption capacity of the at least one branched chained crosslinked polyacrylic acid-type thickening agent. As a result of this high water absorption capacity virtually all of the aqueous vehicle component appears to be held tightly bound to the polymer matrix. Therefore, there appears to be no or substantially no free water present in the invention compositions. This apparent absence of free water (as well as the cohesiveness of the composition) is manifested by the observation that when the composition is poured from a bottle onto a piece of water absorbent filter paper virtually no water is absorbed onto the filter paper over a period of at least several hours or longer and, furthermore, the mass of the linear viscoelastic material poured onto the filter paper will retain its shape and structure. As a result of the absence of loosely bound water, there is virtually no phase separation between the aqueous phase and the polymeric matrix or dissolved solid particles. This characteristic is manifested by the fact that when the subject compositions are subjected to centrifugation, e.g. at 1000 rpm for 30 minutes, there is no phase separation and the composition remains homogeneous. The preferred compositions have remained stable for periods in excess of 4 months and more.

In U. S. Patent 5,064,553, it was stated that to maximize physical (phase) stability, the density of the composition should be controlled such that the bulk density of the liquid phase is approximately the same as the bulk density of the entire composition, including the polymeric thickening agent. This control and equalization of the densities was achieved, according to our earlier invention, by providing the composition with a bulk density of at least 1.32 g/cc. A density of 1.42 g/cc is essentially equivalent to zero air content.

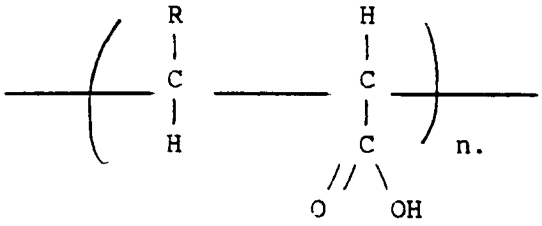
However, it has now been found that air bubble incorporation is not required to achieve stabilization and, in fact, we have been able to prepare stable thickened products with densities as low as 1.28 g/cc. At densities below 1.28 cc/g, however, the flowability of the product tends to be degraded and the large air bubble content tends to cause the composition to be too highly translucent or cloudy to opaque. Therefore, the product density is preferably selected in the range of 1.28 to 1.42 g/cc, especially 1.32 to 1.40 g/cc, and most preferably from 1.35 to 1.40 g/cc.

It has previously been found in connection with other types of thickened aqueous liquid, automatic dishwasher detergent compositions that agglomeration or escape of incorporated air bubbles or the deaeration of the composition could be avoided by incorporating certain surface active ingredients, especially fatty acids and the salts thereof, such as stearic acid, behenic acid, palmitic acid, sodium stearate, aluminum stearate, and the like.

Therefore, in the present invention, the stabilization of air bubbles which may become incorporated into the compositions during normal processing, such as during various mixing steps, is avoided by post-adding the surface active ingredients as well as the organic compound having the previously defined formula R^1COOX to the remainder of the composition, under low shear conditions using mixing devices designed to minimize cavitation and vortex formation.

As will be described in greater detail below the surface active ingredients present in the composition will include the main detergent surface active cleaning agent, and will also preferably include anti-foaming agent (e.g. phosphate ester) and the R^1C00X.

Exemplary of the polycarboxylate type thickening agents are crosslinked polyacrylic acid type thickening agents as 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, crosslinked acrylic acid polymers having an average equivalent weight of 76, and the general structure illustrated by the following formula:



$$\left(-\overset{R}{\underset{H}{C}}- \overset{H}{\underset{C(=O)OH}{C}}- \right)_n .$$

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 crosslinked with polyalkenyl polyether, e.g. 1% of a polyalkyl ether of sucrose having an average of about 5.8 allyl groups for each molecule of sucrose. The preparation of this class of crosslinked 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, CarbopolR Water Soluble Resins.

In general, these thickening resins are preferably copolymers of a water dispersible copolymer of an alpha-beta monoethylenically unsaturated lower aliphatic carboxylic acid crosslinked 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 crosslinked 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, moderately branched chain polyacrylic acid crosslinked with polyalkenyl ether. In addition to the branched nature of these resins, they are also believed to be more highly crosslinked 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 is Carbopol 614 which is the most chlorine bleach stable of this class of thickening resins. Carbopol 614 is also highly stable in the high alkalinity environment of the preferred liquid automatic dishwasher detergent compositions and is 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 moderately branched chain polyacrylic resin, other branched crosslinked 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-hydroxethylacrylate, acrylonitrile, vinyl acetate, ethylene, propylene, and the like, and which have molecular weights of from 500,000 to 10,000,000 and are crosslinked 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 about 5% by weight, or more, in water at 25°C.

At least one thickening agent is preferably used in their crosslinked form. 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 diethyleneglycol, N,N'-methylene-bisacrylamide, 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 to the otherwise generally linear or non-linear polymeric compound while maintaining the crosslinked polymer at least water dispersible and highly water-swellable in an ionic aqueous medium.

The amount of the at least one branched chained crosslinked polymeric acid or other high molecular weight, hydrophilic crosslinked polycarboxylate thickening agent used to impart the desired rheological property of linear viscoelasticity will generally be in the range of from 1.2 to 2.0%, preferably from 1.2 to 1.6%, 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.

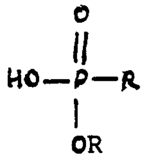
The alkali metal cation will be present in the compositions as the alkali metal cation of the detergent builder salt(s), as well as alkali metal silicate or alkali metal hydroxide components of the compositions. The alkali metal cation may also be present in the compositions as a component of anionic detergent, bleach or other ionizable salt compound additive, e.g. alkali metal carbonate.

Preferred detergent builder salts are sodium tripolyphosphate potassium tripolyphasphate, sodium pyrophosphate and potassium pyrophosphate and mixtures thereof, wherein potassium tripolyphosphate (hydrated or anhydrous) is preferred. The total amount of detergent builder salts is preferably from 10 to 35% by weight, more preferably from 15 to 35%, and most preferably from 18 to 30% by weight of the composition.

When other alkali metal detergent builder salts are present in the formulation, they will usually be present in amounts less than 5% by weight based on the total composition. Other builder salts are illustrated by sodium carbonate, potassium carbonate, alkali metal gluconates, alkali metal phosphonates and alkali metal nitriloacetates, eg nitrilotriacetates.

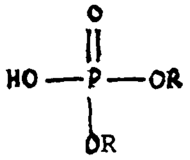
In the case of phosphate free formulations one can employ alternative builders to the polyphosphates such as sodium carbonate, potassium carbonate, zeolite, gluconate or phosphonate.

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 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 builder salts, such as NaTPP which has a water softening effect, may aid in providing a 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



$$\mathrm{HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-R}$$

and especially the alkyl acid phosphate esters of the formula



$$\mathrm{HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-OR}$$

In the above formulas, one or both R groups in each type of ester may represent independently a C_{12}-C_{20} ethoxylated alkyl or alkyl group. The ethoxylated derivatives of each type of ester, for example, the condensation products of one mole of ester with from 1 to 10 moles, preferably 2 to 6 moles, more preferably 3 or 4 moles of ethylene oxide can also be used. Some examples of the foregoing are commercially available, such as the products SAP from Hooker and LPKN-158 from Knapsack. Mixtures of the two types, or any other chlorine bleach stable types, or mixtures of mono- and diesters of the same type, may be employed. Especially preferred is a mixture of mono- and di-C_{16}-C_{18} alkyl acid phosphate esters such as monostearyl/distearyl acid phosphates 1.2/1, and the 3 to 4 mole ethylene oxide condensates thereof. When employed, proportions of 0 to 1.5 weight percent, preferably 0.1 to 0.5 weight percent, of foam depressant in the composition is typical. The weight ratio of detergent active component to foam depressant generally ranges from 10:1 to 1:1 and preferably about 5:1 to 1:1. Other defoamers which may be used include, for example, the known silicones, such as available from Dow Chemicals.

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

Another surprising and unexpected benefit and advantage of the polymeric thickened compositions of this invention is the essentially total masking of any chlorine bleach odor which is characteristic of, for example, the prior known clay thickened products. By virtue of the masking of chlorine bleach odor, it has been found that the subject compositions can be blended with substantially lower amounts of fragrance, e.g. lemon oil fragrance, to achieve the same or superior sensation of smell for the consumer. For instance, as little as 0.05% of lemon fragrance will have the same effect as .12% in clay thickened products.

Furthermore, the addition of fragrance does not adversely affect the stability criteria as previously defined, such as viscosity or phase stability, of the compositions.

Detergent active material which are optionally useful herein should be low-foaming and stable in the presence of chlorine bleach, especially hypochlorite bleach, and for this purpose those of the organic anionic, nonionic, amine oxide, phosphine oxide, sulphoxide or betaine water dispersible surfactant types are preferred, wherein anionic surfactants are most preferred. Particularly preferred surfactants are the linear or branched alkali metal mono- and/or di-(C_8-C_{14})alkyl diphenyl oxide mono- and/or di-sulphates, commercially available for example as DOWFAX (registered trademark) 3B-2 and DOWFAX 2A-1. In addition, the surfactant should be compatible with the other ingredients of the composition. Other suitable organic anionic, non-soap surfactants include the primary alkyl sulphates, alkyl sulphonates, alkyl arylsulphonates and sec.-alkyl sulphates. Examples include sodium C_{10}-C_{18} alkyl sulphates such as sodium dodecyl sulphate and sodium tallow alcohol sulphate; sodium C_{10}-C_{18} alkane sulphonates such as sodium hexadecylbenzene sulphonates.

As other suitable surfactants or detergents, the amine oxide surfactants are typically of the structure R_2R^1NO, in which each R represents a lower alkyl group, for instance, methyl, and R^1 represents a long chain alkyl group having from 8 to 22 carbon atoms, for instance a lauryl, myristyl, palmityl or cetyl group. Instead of an amine oxide, a corresponding surfactant phosphine oxide R_2R^1PO or 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 include lauryl-dimethylamine oxide, myristyldimethylamine oxide, the corresponding phosphine oxides and sulphoxides, and the corresponding betaines, including dodecyldimethylammonium acetate, tetradecyldiethylammonium pentanoate, hexadecyldimethylammonium hexanoate and the like. For biodegradability, the alkyl groups in these surfactants should be linear, and such compounds are preferred.

Surfactants of the foregoing type, all well known in the art, are described, for example, In U.S. Patents 3,985,668 and 4,271,030. If chlorine bleach is not used then any of the well known low-foaming nonionic surfactants such as alkoxylated fatty alcohols, e.g. mixed ethylene oxide-propylene oxide condensates of C_8-C_{22} fatty alcohols can also be used.

The chlorine bleach stable, water dispersible organic detergent-active material (surfactant) will normally be present in the composition in minor amounts, generally about 1% by weight of the composition, although smaller or larger amounts, such as up to 3%, such as from 0.1 to 3%, preferably from 0.1 to 2% by weight of the composition, may be used.

Alkali metal (e.g. potassium or sodium) silicate, which provides alkalinity and protection of hard surfaces, such as fine china glaze and pattern, is generally employed in an amount ranging from 5 to 20 weight percent, preferably 5 to 15 weight percent, more preferably 8 to 12 weight percent in the composition. The sodium silicate is generally added in the form of an aqueous solution, preferably having $Na_2O:SiO_2$ or $K_2O:SiO_2$ ratio of 1:1.3 to 1:2.8, especially preferably 1:2.0 to 1:2.6. At this point, it should be mentioned that many of the other components of this composition, especially alkali metal hydroxide and bleach, are also often added in the form of a preliminary prepared aqueous dispersion or solution. However, unless otherwise noted, when amounts of a particular ingredient are given, the reference is to an active ingredient basis, i.e. does not include the aqueous carrier.

In addition to the detergent active surfactant, foam inhibitor, alkali metal silicate corrosion inhibitor, and detergent builder salts, which all contribute to the cleaning performance, it is also known that the effectiveness of the liquid automatic dishwasher detergent compositions is related to the alkalinity, and particularly to moderate to high alkalinity levels. Accordingly, the compositions of this invention will have pH values of at least 9.5, preferably at least 11 to as high as 14, generally up to 13 or more, and, when added to the aqueous wash bath at a typical concentration level of 10 grams per liter, will provide a pH in the wash bath of at least 9, preferably at least about 10, such as 10.5, 11, 11.5 or 12 or more.

The alkalinity will be achieved, in part, by the alkali metal ions contributed by the alkali metal detergent builder salts, e.g. sodium tripolyphosphate, and alkali metal silicate, however, it is usually necessary to include alkali metal hydroxide, e.g. NaOH or KOH, to achieve the desired high alkalinity. Amounts of alkali metal hydroxide in the range of from 1.2 to 8%, by weight of the composition will be sufficient to achieve the desired pH level.

While as stated above, high alkalinity is desired with regard to improved cleaning performance, it has now additionally been discovered that the pH of the composition during processing is highly important for product stability, e.g. viscosity, and bleach stability and phase stability. Specifically, it has been found that, especially for the polycarboxylate class of thickening agents, the amount of basic neutralizing agent, preferably NaOH, should be sufficient to provide the neutralized thickening agent with a pH of at least 11, preferably at least 11.5. Furthermore, these high alkalinity levels should be maintained throughout the product formulation steps, namely, the pH value of at least 11, preferably at least 11.5, should be maintained during the successive additions of the other ingredients of the composition. If the pH drops to a lower value, there is a loss in viscosity, as well as stability (as manifested by liquid phase separation) over time. Other alkali metal salts, such as alkali metal carbonate may also be present in the compositions in minor amounts, for example from 0 to 9%, preferably 0 to 6%, by weight of the composition to buffer the pH of the composition.

Other inorganic thickening agents such as a finely divided silica, eg Cab-O-Sil from the Cabot Corp. can be used in amounts of 0 to about 8 weight %. Another often beneficial additive for the present liquid automatic dishwasher detergent compositions is a relatively low molecular weight, non-crosslinked polyacrylic acid, such as the Polymer A_3 sold by Rohm and Haas Co., which has a molecular weight of 190,000. The low molecular weight polyacrylic acids can provide additional thickening characteristics, but are also introduced for their ability to function as a builder or chelating agent. In this capacity, the low molecular weight polyacrylic acids can contribute to reduced spotting or streaking and reduced filming on dishes, glassware, pots, pans and other utensils and appliances. Generally, a suitable molecular weight range for the non-crosslinked polyacrylic acid is from 150,000 to 300,000, preferably 150,000 to 250,000, more preferably from 175,000 to 250,000. When present in the formulation, the non-crosslinked polyacrylic acid can be used in amounts up to 10% by weight, preferably from 0 to 9% by weight, more preferably 1 to 8% by weight of the composition.

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. Especially preferred for coloring are the chlorinated phthalocyanines and polysulphides of aluminosilicate which provide, respectively, pleasing green and blue tints. To achieve stable yellow colored products, the bleach stable mixed dyes C.I. Direct Yellow 28 (C.I. 19555) or C.I. Direct Yellow 29 (C.I. 19556) can be added to the compositions. TiO_2 may be employed for whitening or neutralizing off-shades.

The amount of water contained in these compositions should, of course, be neither so high as to produce unduly low viscosity and fluidity, nor so low as to produce unduly high viscosity and low flowability.

The amount of water is readily determined by routine experimentation and generally will range from 30 to 75 weight percent, preferably 35 to 65 weight percent, and most preferably at least 98 weight percent. At least 90 weight present more preferably at least 95 weight percent of the water present in the composition is bound to the high molecular weight polycarboxylate polymer. Preferably, the water should also be deionized or softened.

The manner of formulating the invention compositions is also important. As discussed above, the order of mixing the ingredients as well as the manner in which the mixing is performed will generally have a significant effect on the properties of the composition, and in particular on product density, (by minimization of the incorporation of more or less air), viscosity and physical stability (e.g. phase separation). Thus, according to the preferred practice of this invention the compositions are prepared by forming a dispersion of the polycarboxylate type thickeners in heated water, e.g. 35°C to 60°C (95°F to 140°F), preferably 40°C to 50°C (104°F to 122°F), under moderate to high shear conditions, neutralizing the dissolved polymer with an alkali metal hydroxide or an alkali metal silicate to a pH of at least 11, preferably at least 11.5, such as from 11.5 to 13.0, to cause gelation. After transferring the thickener dispersion to a main mixing tank, processing is continued by introducing, while continuing mixing, the detergent builder salts, alkali metal silicates, chlorine bleach compound and remaining detergent additives, including any previously unused alkali metal hydroxide, if any, other than the surface-active compounds. All of the additional ingredients can be added simultaneously or sequentially, with mixing continued for from 2 to 10 minutes for each ingredient, although it is not necessary to complete the addition of one ingredient before beginning to add the next ingredient. Furthermore, one or more of these ingredients can be divided into portions and added at different times. These mixing steps should also be performed under moderate to high shear rates to achieve complete and uniform mixing. These additional ingredient mixing steps may be carried out at room temperature, but preferably the elevated temperature of the thickener slurry is maintained. The composition may be allowed to age, if necessary, to cause unintentionally dissolved or dispersed air to dissipate out of the composition.

The remaining surface active ingredients, including the anti-foaming agent, organic detergent compound, and the R^1C00X organic compound as previously defined are post-added to the previously formed mixture in the form of an aqueous emulsion (using from 1 to 10%, preferably from 2 to 4% of the total water added to the composition other than water added as carrier for other ingredients or water of hydration) which is pre-heated to a sufficient temperature (120° to 170°F) (49 to 77°C) to form a milky emulsion. If care is taken to avoid excessive air bubble incorporation during the gelation step or during the mixing of the detergent builder salts and other additives, for example, by operating under vacuum, or using low shearing conditions, or special mixing apparatus, etc., the order of addition of the surface active ingredients should be less important.

In accordance with an especially preferred embodiment, the thickened linear viscoelastic aqueous automatic dishwasher detergent composition of this invention includes, on a weight basis:

(a)(i) 10 to 35%, more preferably 10 to 25% of at least one detergent builder, preferably an alkali polyphosphate;

(b) 0 to 25, more preferably 8 to 20%, of alkali metal silicate;

(c) 0 to 10%, more preferably 1.0 to 8%, of alkali metal hydroxide;

(d) 0 to 3%, more preferably 0.1 to 3%, of chlorine bleach stable, water-dispersible, or water soluble organic detergent active material, preferably non-soap anionic detergent;

(e) 0 to 1.5%, more preferably 0.05 to 1.5%, of chlorine bleach stable foam depressant;

(f) chlorine bleach compound in an amount to provide 0.2 to 5%, preferably 0.8 to 2.5%, of available chlorine;

(g) at least one branched chain, crosslinked water-dispersible polyacrylic acid thickening agent having a molecular weight of from 750,000 to 4,000,000. more preferably 800,000 to 3,000,000, in an amount sufficient to provide a linear viscoelasticity to the formulation, or preferably from 0.1 to 2%, most preferably from 0.4 to 1.5% and still more preferably from 0.4 to 1.0%;

(h) 0 to 10%, preferably 1 to 8%, especially 2 to 6% of a non-crosslinked polyacrylic acid having a molecular weight in the range of from about 150,000 to 300,000;

(i) 0.00 to 5% of an organic compound having the formula R^1C00X wherein x represents a hydrogen atom or an alkali metal cation and R^1 represents a phenyl group or a substituted phenyl group; and

(j) water, preferably from 30 to 75%, more preferably from 35 to 65% wherein at least 90 weight percent of the water is bound to the high molecular weight polymer; and wherein the composition has a bulk density from 1.28 to 1.47 g/cc, and more preferably from 1.32 to 1.42 g/cc, most preferably from 1.35 to 1.35 to 1.42 g/cc.

The compositions will be supplied to the consumer in suitable dispenser containers preferably formed of molded plastic, especially polyolefin plastic, and most preferably polyethylene, for which the invention compositions appear to have particularly favorable slip characteristics. In addition to their linear viscoelastic character, the compositions of this invention may also be characterized as pseudoplastic gels which are typically near the borderline between liquid and solid viscoelastic gel, depending, for example, on the amounts and types of the polymeric thickeners. The invention compositions can be readily poured from their containers at a rate of at least 225 grams/minute through a 0.375 inch (8.45 mms) opening, when the container is aligned parallel to a vertical axis and without any shaking or squeezing, i.e. have a sufficiently low yield stress value to flow under their own weight (gravity), although squeezable containers are often convenient and accepted by the consumer for gel-like products.

The liquid aqueous linear viscoelastic automatic dishwasher compositions of this invention are readily employed in known manner for washing dishes, other kitchen utensils and the like in an automatic dishwasher, provided with a suitable detergent dispenser, in an aqueous wash bath containing an effective amount of the composition, generally sufficient to fill or partially fill the automatic dispenser cup of the particular machine being used.

The invention also provides a method for cleaning dishware in an automatic dishwashing machine with an aqueous wash bath containing an effective amount of the liquid linear viscoelastic automatic dishwasher detergent composition as described above. The composition can be readily poured from the polyethylene container with little or no squeezing or shaking into the dispensing cup of the automatic dishwashing machine and will be sufficiently viscous and cohesive to remain securely within the dispensing cup until shear forces are again applied thereto, such as by the water spray from the dishwashing machine.

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.

DETAILED DESCRIPTION OF THE INVENTION

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

Example I

The following formulations A-H were prepared as described below:

TABLE I

Ingredient	A	B	C	D	E	F
DI Water	q.a	q.a	q.a	q.a	q.a	q.a
Carbopol 614	1.3	1.3	1.3	1.3	1.3	1.3
Sodium Silicate	20.83	20.83	20.83	20.83	21.0	21.0
Caustic (50%)	4.5	4.5	4.5	4.5	4.5	4.5
KTPP	20.35	20.35	20.35	20.35	20.00	20.00
Na-TPP	5.26	5.26	2.00	5.26	2.00	2.00
Phosphate ester (LPKN)	-	0.16	0.16	0.16	0.16	0.16
Dowfax 3B-2 (45%)	-	0.80	-	-	-	-
NaOCl (13%)	9.2	9.2	9.2	9.2	10.0	9.5
Color	0.003	0.003	0.003	0.003	0.003	0.003
Fragrance	0.03	0.03	0.03	0.03	0.03	0.03
Sodium benzoate	-	-	-	0.85	0.90	3.50
Polymer-A_3 (25%)$^+$	-	-	-	-	2.00	-

$^+$ Rohm and Haas - polyacrylate with molecular wt. 190,000

Formulations A - F are prepared by first forming a uniform dispersion of the Carbopol thickeners in about 97% of the water of the total formula water. The Carbopols are slowly added by sprinkling them into the vortex of previously colored deionized water preheated to a temperature of 105°F (41°C) using a mixer equipped with a Premier blade, with agitation set at a medium shear rate, as recommended by the manufacturer. After mixing for about 15 minutes, the dispersion is then neutralized by addition, under the same mixing, of the caustic soda (50% NaOH) component until a thickened product of gel-like consistency is formed (about 10 minutes).

To the resulting gelled dispersion the silicate, sodium tripolyphosphate (NaTPP), the surfactant emulsion (described below), bleach and color, are added sequentially, in the order stated, with the mixing continued at medium shear for several minutes before adding the next ingredient. After the addition of the surfactant emulsion (at 160°F) (71°C), the mixture is cooled to from 90°-95°F (32-35°C) before the bleach is added.

Separately, the surfactant emulsion of the phosphate anti-foaming agent (LPKN), detergent (Dowfax 3B2) and the organic compound of the formula R^1C00X such as sodium benzoate is prepared by adding these ingredients to the remaining 3% of water and heating the resulting mixture to a temperature in the range of 160°F (71°C). The Polymer A_3 may be added at this stage.

Ease of dispensability of the formulations was evaluated by the following general procedure. A 64 oz. (1.8 kilograms) polyethylene bottle with a cap orifice size of 0.375" (8.45 mms diameter) was filled with 300 gms of test sample and left on the bench top for about 10 minutes. The bottle was then suspended perpendicular to the plane of the bench with the cap facing downward. The orifice cap was then opened and the product was allowed to drain under gravitational force. The flow rate (i.e., amount of product dispensed/minute) was used to determine the ease of product dispensability. The results are summarized in Table III. The rate of dispensability of the present invention (B-H) is superior to the prior art example A.

The ease of dispensability correlates very well to the thixotropic index (TI) of the samples. The latter being defined as the ratio of Brookfield viscosity of the sample at 3 rpm and 30 rpm. The TI of the formulations are shown in Table II. For ease of dispensability, the preferred range of TI is 4 to 5.7.

TABLE II

Thixotropic index and stability of benzoate compositions				
Composition	Stability			Thixotropic Index
	140 ° F* (60 ° C)	120 ° F** (49 ° C)	RT	
Control[x]	0.0	0.0	0.0	6.00
A	0.0	0.0	0.0	5.50
B	0.0	0.0	0.0	4.80
C	0.0	0.0	0.0	5.70
D	0.0	0.0	0.0	5.4
E	0.0	0.0	0.0	4.4
F	0.0	0.0	0.0	3.5

* Control
* Minimum 3 Days
** Minimum 1 Week

TABLE III

Prototype	Flow rate (gms/minute)
Control	159
A	249
B	262
C	231
D	251
E	271
F	284

Claims

1. A linear viscoelastic aqueous liquid automatic dishwasher detergent composition containing a polymeric thickener characterised in that it contains an organic compound containing a carboxylic acid group such as to increase the rate of flow of the composition from a container having an outlet opening 8.45 mms in diameter, and in that the polymeric thickener is a crosslinked polyacrylic acid present in an amount sufficient to generate a three-dimensional network having viscoelastic properties.

2. A composition as claimed in claim 1 characterised in that the organic compound has the formula R^1COOX wherein X represents a hydrogen atom or an alkali metal cation and R^1 represents a phenyl group or a substituted phenyl group.

3. A composition as claimed in claim 1 or claim 2 characterised in that it is free from any fatty acid moiety.

4. A linear viscoelastic aqueous liquid automatic dishwasher detergent composition comprising water, optionally from 0.005 to 0.2 of a compound having the formula R^1COOX wherein X represents a hydrogen atom or an alkali metal cation and R^1 represents a phenyl group or a substituted phenyl group, from 0 to 5% by weight of a chlorine bleach stable, water dispersible or soluble organic detergent, from 5 to 40% by weight of at least one alkali metal tripolyphosphate, up to 20% by weight of a chlorine bleach compound, and at least 1.2, preferably 1.2 to 2.0 weight percent of at least one branched crosslinked polymeric, preferably polycarboxylate-type, thickening agent having a molecular weight of at least 1,000,000.

5. A composition as claimed in any one of the preceding claims characterised in that it comprises an alkali metal silicate.

6. A composition as claimed in any one of the preceding claims characterised in that the crosslinked polymeric thickening agent is a crosslinked polyacrylic acid.

7. A composition as claimed in any one of the preceding claims characterised in that the said R^1COOX is benzoic acid or sodium benzoate or a mixture thereof.

8. A composition as claimed in any one of the preceding claims characterised in that it includes an anti-foaming agent.

9. A linear viscoelastic aqueous liquid automatic dishwasher detergent comprising, approximately

(a) 0 to 35 wt% of at least one polyphosphate detergent builder;
(b) 5 to 20 wt% alkali metal silicate;
(c) 0 to 8 wt% alkali metal hydroxide;
(d) 0 to 3 wt% chlorine bleach stable, water-dispersible organic detergent active material;
(e) 0 to 1.5 wt% chlorine bleach stable foam depressant;
(f) chlorine bleach compound in an amount to provide 0.2% to 4% of available chlorine;
(g) 1.2 to 2 wt% of at least one branched chain hydrophilic crosslinked high molecular weight polycarboxylate thickening agent to provide the said linear viscoelastic property to the said composition;
(h) 0 to 5 weight % of an organic compound having the formula R^1COOX wherein x represents a hydrogen atom or an alkali metal cation and R^1 represents a phenyl group or a substituted phenyl group;
(i) 0 to 10 wt% of a non-crosslinked polyacrylic acid having a molecular weight of from 150,000 to 300,000; and
(j) water, wherein the said composition has a bulk density of from 1.28 g/cc to 1.42 g/cc.

10. A composition as claimed in claim 9 characterised in that it comprises, approximately

(a) 18 to 30 wt% alkali metal tripolyphosphate;
(b) 8 to 18 wt% alkali metal silicate;
(c) 1.2 to 7 wt% alkali metal hydroxide;
(d) 0 to 2 wt% chlorine bleach stable, water-dispersible, low-detergent active material;
(e) 0 to 0.5 wt% chlorine bleach stable foam depressant;
(f) chlorine bleach compound in an amount to provide 0.8 to 2.5% of available chlorine;
(g) 1.2 to 2.0 wt% of at least one crosslinked polyacrylic acid having a molecular weight of from 1,000,000 to 4,000,000;
(h) 0 to 3.0 weight % of an organic compound having the formula R^1COOX wherein x represents a hydrogen atom or an alkali metal cation and R^1 represents a phenyl group or a substituted phenyl group;
(i) 0 to 8 wt% of a non-crosslinked polyacrylic acid having a molecular weight of from 150,000 to 300,000; and
(j) water, at least 90 weight percent of the said water being bound to the said crosslinked thickening agents.

11. A composition as claimed in any one of the preceding claims characterised in that the water is substantially bound.

12. A method for preparing a thickened stable aqueous automatic detergent dishwashing composition which comprises the steps of

I.

(a) fully hydrating a blend of a branched chain crosslinked high molecular weight polycarboxylate thickener and a more highly branched chain crosslinked high molecular weight polycarboxylate thickener by slowly adding the blend of the said thickeners to water preheated to a temperature of from 95 to 140°F (35 to 60°C) while moderately agitating the mixture,
(b) slowly adding a neutralizing agent comprising caustic soda to the mixture from (a) while continuing agitation to obtain a dispersion of the neutralized blend of thickeners;

II.

(c) forming an aqueous mixture of a chlorine-bleach stable, water dispersible or water soluble detergent active material, an organic compound having the formula R^1COOX wherein x represents a hydrogen atom or an alkali metal cation and R^1 represents a phenyl group or a substituted phenyl group, and optionally a foam depressant;

(d) heating the mixture in (c) to a temperature higher than 140°F (60°C) and mixing until a homogeneous smooth surfactant premix emulsion is obtained;

III.

(e) uniformly mixing sodium tripolyphosphate with the dispersion,

(f) uniformly mixing the heated premix surfactant emulsion (d) with the mixture (e),

(g) cooling the mixture (f) to 95°F (35°C) or lower, and

(h) adding bleach to the mixture (g).

13. A method as claimed in claim 10 characterised in that the amount of neutralizing agent is sufficient to raise the pH of the polycarboxylate dispersion to at least 11, and maintain the pH in each subsequent step at at least 11.

14. A method as claimed in claim 11 characterised in that the pH is 11.5 or more.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 30 3608

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-0 398 021 (COLGATE - PALMOLIVE CO.)	1,5,6, 8-10	C11D17/00 C11D3/37
A	* the whole document * ---	4,11-13	C11D3/20
D,X	US-A-4 859 358 (S.M. GABRIEL ET AL.)	1,5,6, 8-10	
	* the whole document * ---		
X	GB-A-2 219 596 (THE PROCTER & GAMBLE CO.)	1,5,6, 8-10	
	* claims * ---		
D,X	US-A-4 836 948 (R. CORRING)	9,10	
D,A	* the whole document * ---	1,4-6,8	
A	EP-A-0 317 066 (THE CLOROX CO.)	1,2,4-7, 9,10	
	* the whole document * ---		
A	EP-A-0 342 786 (THE CLOROX CO.)	1,2,4,5, 7,9,10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
	* page 5, line 50 - page 8, line 13 * * page 12, line 45 - page 13, line 14; claims 1-3,16,19,22 * ---		C11D
A	EP-A-0 298 172 (THE DOW CHEMICAL CO.) * page 5, line 25 - line 30; claims; examples * ---	1,2,4	
P,X	EP-A-0 446 761 (COLGATE - PALMOLIVE CO.)	1,5,6, 8-10	
P,A	* the whole document * -----	4,11-13	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 OCTOBER 1992	SERBETSOGLOU A.

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
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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