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(54) Title: STRUCTURED SILICATES AND THEIR USE IN AUTOMATIC DISHWASHERS

(57) Abstract

A shear thickening composition having a viscosity at room temperature at 12 to 80 pascal seconds which comprises by weight 10 to 45 % of an alkali metal silicate; 1 to 45 % of an inorganic or organic compound having an alkali metal cation; 0 to 5,0 % of at least one organic detergent active material; and water.

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STRUCTURED SILICATES AND THEIR USE IN AUTOMATIC DISHWASHERS

Field of Invention

The invention relates to an aqueous liquid composition which is especially useful as detergent compositions. If the water content is low enough, shear thickening is exhibited.

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 two major problems, product phase instability shear sensitivity 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 Dixit, et al., U.S. Patent 5,053,158; Prince, U.S. Patent 5,130,043; Baxter, U.S. Patent 4,950,416; Wise, U.S. Patent 4,941,988; Cilley, U.S. Patent 4,933,101; Colarusso, U.S. Patent 4,927,555; Gabriel, U.S. Patent 4,859,358; Roselle, U.S. Patent 4,824,590; 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 4,521,332; Laitem, U.S. Patent 4,753,748; Sabatelli, U.S. Patent 3,579,455; Hynam, U.S. Patent 3,684,772; U.S. Patent 4,836,946; Ahmed et. al., U.S. Patent

4,889,653; Smeets, U.S. Patent 3,720,621; U.S. Patent 4,836,948; and U.K. Patent Applications GB 2,116,199A and GB 240,450A.

While the compositions disclosed in the above patents provide satisfactory solutions to the problems of phase instability and bottle residue, as well as cup leakage, it has now been found that under some storage/handling conditions and/or processing conditions, additional improvements would be desirable. Specifically, if the viscoelastic compositions are subjected to repeated heating and cooling cycles, growth of crystals and product thinning and/or precipitate formation has been observed. Chemical analysis of the precipitated crystals has shown that these crystals are comprised predominantly of sodium pyrophosphate. In addition, it appears that the crystals tend to become entangled with the polymeric thickener which tendency is presumed to account for the thinning (shear sensitivity) or aqueous phase separation which has been observed in conjunction and crystal formation and precipitation.

The prior art teaches compositions that exhibit thixotropic properties. These prior art compositions exhibit shear thinning or a decrease in viscosity as the shear rate is increased. The compositions of the instant invention do not shear thin as the shear rate increases but the instant compositions shear thicken (viscosity increases) as shear rate increases.

United States patent 4,575,530 (March 11, 1986) describes hydrocarbon solution additives which are polyampholytes which incorporates cationic and anionic moieties on the same polymeric backbone. These hydrocarbon solutions have shear thickening properties.

U.S. patent 4,536,539 (August 20, 1985) claims include increasing the viscosity of water under increasing shear rates (22.0 - approaching 100 sec^{-1}). This shear thickening behavior is primarily attributed to the increase in apparent molecular weight of the interpolymer complex through formation of intermolecular ionic linkages.

U.S. Patent 4,941,988 to Wise discloses at Example 1 a composition containing 72.83 wt. % of sodium silicate (47.3% a.i. in aq. soln.), 1.36 wt. % sodium aluminate,

and water, but there is no indication the material was shear thickening and it does not appear to be such.

Various attempts have been made to develop thickened, highly viscous bleach cleaning compositions for applications on non-horizontal surfaces, and to provide

Various attempts have been made to develop thickened, highly viscous bleach cleaning compositions for applications on non-horizontal surfaces, and to provide compositions wherein splashing is minimized. Numerous approaches to thickening a cleaning composition are known and include increasing the concentration of dissolved components, adding suspended solids, modifying characteristics of the dissolved components to create liquid crystal or gel phases, or by adding polymeric organic thickening agents.

For various reasons, the prior art thickened compositions are not commercially viable. In many instances, thickening is insufficient to provide the desired residence time on non-horizontal surfaces. Adding components, and/or modifying characteristics of dissolved components often creates additional problems with the composition, such as syneresis, which require adding further components in an attempt to correct these problems. A drawback that has hampered prior art polymer thickened hypochlorite bleaching compositions is the tendency of the hypochlorite to oxidize the polymer, reducing or destroying its thickening capability. Polymer-thickened hypochlorites are disclosed or described in several references. U.S. Patent 4,839,077 teaches a polymeric thickened bleach composition which overcomes the deficiency of polymer oxidation. U.S. Pat. No. 4,011,172 issued to Marsan et al discloses clay thickened hypochlorite and suggests that polyacrylamides may also be suitable. Briggs, U.S. Pat. No. 3,663,442 discloses a composition comprising bleach and a styrene/acrylic acid polymer which is formulated as an insoluble particulate for opacification rather than thickening. Rupe et al, U.S. Pat. No. 4,116,851 shows a clay thickened hypochlorite bleach which could include polymeric thickening agents such as polystyrene, polypropylene, polyethylene or copolymers of styrene with e.g., acrylate, maleate or vinyl acetate. Such polymers are disclosed in particulate form,

however, and apparently thicken only in conjunction with the inorganic clays. U.S. Pat. No. 4,438,016 issued to Kiewert et al discloses a hypochlorite cleanser containing amine oxides and paraffin sulfonates, and thickened by calcium aluminum silicates and optionally by acrylate or methacrylate copolymers. Zimmerer et al, U.S. Pat. No. 3,393,153 shows non-thickened hypochlorite bleach compositions which stably suspends optical brighteners aided by various insoluble polymers. Sabatelli, U.S. Pat. No. 4,147,650 shows a hypochlorite solution thickened with a combination of metasilicates and polyacrylate or polymethacrylate having a high average molecular weight, as typical of the prior art. Hynam et al, U.S. Pat. No. 3,684,722 discloses a thickened bleaching composition of amine oxides or betaines, an alkali-metal soap, an alkali metal hypochlorite and, optionally, caustic. Hynam et al mentions that polymers such as polyacrylates were tested for their ability to thicken the hypochlorite, but no lasting thickening was achieved. French Pat. No. 78 23943 describes a non-surfactant, polymeric thickened hypochlorite composition. This patent illustrates the ineffectiveness of polymeric thickeners of the art, as high levels of polymers such as polyacrylate (25% or more) are required to attain a moderate, one hundred centipoise (cP) thickening. Polyacrylates are generally shown in the art cited above to be unstable in hypochlorite solutions. Other references, such as Joy, U.S. Pat. No. 4,229,313 disclose surfactant thickened bleach compositions.

None of the compositions disclosed in the aforementioned prior art appear to possess shear thickening properties. These compositions of the prior art are shear thinning as the rate of shear is increased.

The chemistry of silica and silicate colloids has been studied, and some of the work is reflected in Iler, "The Colloid Chemistry of Silica and Silcates" (Cornell Univ. Press 1955). There is, however, no apparent reference to shear thickening silicate formulations in the reference.

U.S. Patent 4,941,988 to Wise discloses at Example 1 a composition containing 72.83 wt.% of sodium silicate (47.3% a.i. in aq. soln.), 1.36 wt.% sodium aluminate,

and water, but there is no indication the material was shear thickening and it does not appear to be such.

This invention also relates to liquid, aqueous, stable, effective, safe, detergent prespotter cleaning compositions for fabrics which have shear thickening properties and are commonly referred to as prespotters for cleaning of fabrics. The compositions are physically stable, do not separate, whereby the user is assured of the optimum performance to be expected from the various components and their amounts and ratios with respect to one another.

This invention relates to liquid, aqueous, stable, effective, safe, non-scratching hard surface cleaning compositions which have shear thickening properties and are commonly referred to as scouring cleansers. The compositions are physically stable, do not separate, whereby the user is assured of the optimum performance to be expected from the various components and their amounts and ratios with respect to one another. These compositions are also safe and do not scratch the usual surfaces to be cleaned, such as glass, porcelain, ceramic, plastic, metal, wood, painted wood (enamelled and lacquered). The compositions of the instant invention because of their dilatant properties are especially useful in the cleaning of vertical surfaces.

The art is, of course, replete with liquid scouring compositions alleged to perform in a safe and effective manner, while others are stated to be physically and chemically stable.

Some examples or prior art scouring compositions include U.S. Patent 4,005,027 which describes compositions which include clay and insoluble abrasive. Only inorganic abrasives are shown and nonionics are not used. The compositions include surfactants which are bleach stable. It is alleged that the products are physically stable and also do not "appreciably run along vertical surfaces" (column 10, lines 45-47). Such stability is a manifestation of a falso body fluid formed when using the smectite and attapulgite clays necessary in such compositions. The compositins of U.S. Patent 4,116,849 are very similar to those in U.S. Patent 4,005,027. In addition, U.S. Patent 4,116,849 discloses thickening agents instead of the preferred

smectite and attapulgite clays, such as collodial silica, polystyrenes, sulfonated polystyrenes, polyethylene, oxidized polyethylenes, polypropylene, copolymers of styrene with methacrylic acid, methyl or ethyl acrylate, vinyl acetate, among others; patentee states that "...ethoxylated nonionic surfactants are to be avoided." Neither of these two patents disclose soaps or fatty acids as suitable materials as well. U.S. Patent 4,240,919 describes compositions of multivalent stearate soap, water and water-insoluble abrasive. Various abrasives are disclosed and among the "organic" types are "melamine, urea formaldehyde resins, ground rigid polymeric materials, such as polyurethane foam..." (column 3, lines 10-12). Optionally, there may be present "substantially any surfactant materials which are compatible with the other components in the composition of the present invention..." These include wate-soluble anionic, nonionic, amphoteric, cationic and zwitterionic surfactants." (column 3, lines 57-62). Further reference is made to U.S. Patents 4,051,056 (expanded perlite as abrasive), 4,457,856 (polyacrylate abrasive), German 1,956,616 (polyvinyl chloride as abrasive) and 3,645,904 (skin cleanser containing polymer abrasive material).

All of the compositions disclosed in the aforementioned prior art do not possess shear thickening properties. These compositions of the prior art are shear thinning as the rate of shear is increased. In other words, as the shear rate is increased as inthe process of scrubbing, the viscosity of the composition will decrease. The compositions of the instant invention exhibit shear thickening properties which means that as the shear rate is increased the compositions will shear thicken. In a scrubbing process which causes an increase in the shear rate, the viscosity of the composition will increase and the composition will exhibit gel-like properties. This shear thickening of the compositions of the instant invention make them especially useful on vertical surfaces because of their tendency not to run off of the vertical surface which is being cleaned as compared to the prior art compositions.

United States Patent 4,575,530 (March 11, 1986) describes hydrocarbon solution additives which are polyampholytes which incorporates cationic and anionic

moieties on the same polymeric backbone. These hydrocarbon solutions have shear thickening properties.

U.S. Patent 4,536,539 (August 20, 1985) claims include increasing the viscosity of water under increasing shear rates (22.0 - approaching 100 sec-1). This shear thickening behavior is primarily atributed to the increase in apparent molecular weight of the interpolymer complex through formation of intermolecular ionic linkages.

Our patent teaches that these thickened silicates show shear thickening (dilatency), an increase in viscosity as shear rate is increased. Furthermore, the viscosity values at each shear rate are independent of the timescale of the experiment. Once the shear rate is applied, the viscosity reaches a steady value after a few seconds up to several minutes. Shear thickening occurs when the applied shear forces predominate the interparticle forces. The shear forces change the dispersion from a certain degree of order to clusters of particles. Shear thickening behavior is dependent on particle shape, size and size distribution; particle volume fraction type and strength of inter-particle interaction; continuous phase viscosity; and the experimental parameters characterizing the shear thickening. These paramets include the type, rate, and duration of the applied shear deformation.

This invention also relates to a paste type, effective, safe, detergent cleaning compositions which have shear thickening properties. The compositions are physically stable, do not separate, whereby the user is assured of the optimum performance to be expected from the various components and their amounts and ratios with respect to one another.

Summary of the Invention

We have discovered thickened silicates described below which show shear thickening (dilatancy), an increase in viscosity as shear rate is increased. Once the shear rate is applied, the viscosity reaches a steady value after a few seconds up to several minutes. The shear forces appear to change the dispersion from a certain degree of order to clusters of particles. Shear thickening behavior appears to be

dependent on particle shape, size and size distribution; particle volume fraction; type and strength of inter-particle interaction; continuous phase viscosity; and the experimental parameters characterizing the dilatancy. These parameters include the type, rate and duration of the applied shear deformation.

According to the present invention there is provided an improved aqueous liquid automatic dishwasher detergent composition that has shear thickening properties (dilatancy) which means that the composition will show an increase in viscosity as the shear rate increases. The composition exhibits substantially indefinite stability against phase separation or settling of dissolved particles under high and low temperature conditions, low levels of bottle residue, relatively high bulk density. The compositions also show 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 10%.

The present invention can be accomplished, for example, by the use of an aqueous alkali metal silicate such as sodium or potassium silicate and alkali metal builder salt such as tripolyphosphates, pyrophosphates, carbonates, citrates, phosphinates and gluconates in a weight ratio of 1:1 to 100:1. Thixotropic thickeners, such as inorganic clays, polymers or fatty acids may be added, but are not necessary.

Accordingly, in one aspect, the present invention provides an improved automatic dishwasher detergent composition comprising water from 0.0 to 5% by weight of low foaming chlorine bleach stable, water dispersible automatic dishwasher organic detergent, from 1 to 45% by weight of alkali metal builder salt, 10 to 45 weight percent of alkali metal silicate, from 0 to 20% by weight of a chlorine bleach compound.

We have discovered thickened silicates described below which show shear thickening, that is, an increase in viscosity as shear rate is increased. Shear thickening behavior appears to be dependent on particle shape, size and size distribution; particle volume fraction; type and strength of inter-particle interaction;

continuous phase viscosity; and the experimental parameters characterizing the shear thickening. These parameters include the type, rate, and duration of the applied shear deformation.

The present invention relates to a shear thickening aqueous cleaning composition comprising water, at least one alkali metal silicate, and at least one halogen containing compound such as a bleach, and at least one inorganic or organic compound containing an alkali metal cation, and optionally at least one surfactant. In a cleaning process which causes an increase in the shear rate, the viscosity of the composition will increase and the composition will exhibit gel-like properties. This shear thickening property of the compositions of the instant invention make them especially useful on vertical surfaces because of their tendency not to run off of the vertical surface which is being cleaned as compared to the prior art compositions. Also, they tend not to splash, a consumer advantage of highly alkaline compositions. Shear thickening effect increases as water concentration in the composition decreases.

The present invention also relates to liquid, aqueous, stable, effective, safe non-scratching hard surface cleaning compositions which have shear thickening properties and are commonly referred to as scouring cleansers. The compositions are physically stable, do not separate, whereby the user is assured of the optimum performance to be expected from the various components and their amounts and ratios with respect to one another. These compositins are also safe and do not scratch the usual surfaces to be cleaned, such as glass, porcelain, ceramic, plastic, metal, wood, painted wood (enamelled and lacquered). The compositions of the instant invention because of their shear thickening properties are especially useful in the cleaning of vertical surfaces.

The present invention also relates to a paste type composition having a viscosity at room temperature at a shear rate of 22 sec-1 of 12 to 80 pascal seconds and a viscosity at room temperate at 5 sec-1 shear rate of 15 to 90 pascal seconds which comprises by weight percent of: 10-60% of an alkali metal silicate 0.1 to 40% of

an organic or inorganic compound having an alkali cation or an organic compound having at least one hydroxyl group, 0 to 15% of a detergent active material and optionally sufficient chlorine bleach to provide 0.2 to 4.0 wt. % of available chlorine and the balance being water.

Brief Description of the Drawings

Figure 1 graphically shows viscosity versus time for Sample N in Example 2 at a constant shear rate of 5 sec^{-1} as measured on a Carri-Med CSL 100 rheometer under the conditions described in Example 1.

Figure 2 graphically shows Torgue versus time for Sample L in Example 2 as measured on a HATD Digital Brookfield Viscometer using Spindle #7 at room temperature (24°C).

Detailed Description and Preferred Embodiments

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

The objects of this invention are obtained in accordance with the following description wherein the liquid, shear thickening, aqueous, cleansing composition comprises at least one alkali metal silicate, at least one inorganic or organic compound containing an alkali metal cation, at least one compound containing an active halogen and water and, optionally, at least one anionic surfactant and/or at least one nonionic surfactant (i.e., at least one detergent active material).

The advantageous characteristics of the compositions of this invention, include physical stability, as manifested by little or no phase separation, low spotting and filming, dirt residue removal, and consistency in product characteristics and performance, and superior aesthetics. These characteristics are believed to be attributed to several interrelated factors such as dissolved solids, that is low

undissolved particulate content, product density and shear thickening rheology. These facts are, in turn, dependent on several critical compositional components and processing conditions of the formulations, namely, (1) a mixture of an alkali metal silicate and an inorganic or organic compound containing an alkali metal cation in a weight ratio of 1:1 to 100:1; (2) a product bulk density of at least 1.28 g/cc, especially at least 1.32 g/cc, and (3) maintaining the pH of the detergent composition at least at 11 preferably at least at 11.5.

The compositions of this invention are characterized by their low bottle residue and cup leakage of less than 10 wt. %, more preferable less than 8 wt. % and most preferably less than 6 wt.%. Specifically, bottle residues, under the usual use conditions, will be no more than 8 to 10%.

In accordance with an embodiment of the invention, the shear thickening aqueous automatic dishwasher detergent composition of this invention includes, on a weight of active ingredient (i.e., net of aqueous solution) basis:

(a) 10 to 50%, preferably 15 to 40%, alkali metal silicate;

(b) 1 to 45%, preferably 2 to 30% of an inorganic or organic compound having an alkali metal cation, preferably a detergent builder salt;

(c) 0 to 8%, more preferably, 0.1 to 6% alkali metal hydroxide;

(d) 0 to 5%, preferably 0.1 to 3%, more preferably 0.5 to 2% chlorine bleach stable, water-dispersible, low-foaming organic detergent active material, preferably non-soap anionic detergent;

(e) 0 to 1.5%, preferably 0.1 to 0.5%, chlorine bleach stable foam depressant;

(f) optionally, chlorine bleach compound in an amount to provide 0.2 to 4% preferably 0.8 to 1.6% of available chlorine; and

(g) water, wherein the composition has a complex viscosity at room temperature 2 sec-1 of 12 to 100 pascal seconds, more preferably 15 to 80 pascal seconds.

The aqueous, shear thickening, cleaning compositions of the present invention also comprise approximately by weight (i.e., weight % of active ingredient--net of aqueous solution):

(a) 10 to 50% of at least one alkali metal silicate, preferably 15 to 40%;

(b) 0.1 to 15% of at least one halogen containing compound, preferably 0.2 to 10%;

(c) 0.1 to 50% of at least one inorganic compound or organic compound containing an alkali metal cation, preferably 0.5 to 35%;

(d) 0 to 15% of at least one detergent active material, preferably from 1 to 10%, most preferably from 1 to 5%; and

e) water, wherein, preferably, the composition has a viscosity at room temperature at a shear rate of 2 sec^{-1} of 0.1 to 1000 pascal seconds, more preferably from 0.5 to 300 pascal seconds.

This invention also relates to liquid, aqueous, stable, effective, safe, detergent prespotter cleaning compositions for fabrics which have shear thickening properties and are commonly referred to as prespotters for cleaning of fabrics. The compositions are physically stable, do not separate, whereby the user is assured of the optimum performance to be expected from the various components and their amounts and ratios with respect to one another.

The liquid, shear thickening non-scratching, aqueous, scouring cleansing composition of the instant inventor comprises an aqueous alkali metal silicate, an inorganic or organic compound containing an alkali metal cation or an organic compound containing at least one hydroxyl group and water and, optionally, a fatty acid and/or fatty acid soap, a non-soap a anionic surfactant, nonionic surfactant, at least one electrolyte and at least one particulate abrasive.

The paste type shear thickening detergent cleansing composition of the instant invention comprises an alkali metal silicate, an inorganic or organic compound containing an alkali metal cation and water and, optionally, a non-soap anionic

surfactant and/or a nonionic surfactant, and optionally, at least one electrolyte and an alkali metal hydroxide.

Silicates

The alkali metal silicate employed in the instant invention is selected from the group consisting of lithium silicate, potassium silicate and sodium silicate, wherein the alkali metal silicate has a concentration in the composition of at least 10 wt. %, and preferably from 15 to 40 wt.%. Sodium or potassium silicates of Alk. $Metal_2O(xSiO_2)$ are preferred, including both hydrated and anhydrous. When sodium silicate is used, the value of x should preferably be at least 2.88, and the aqueous solution of the silicate should preferably be less than 61% by weight water or more than 39% by weight of the sodium silicate. If potassium silicate is used, the value of x should preferably be at least 2.1, and the aqueous content of a solution should preferably be less than 66% by weight.

The shear thickening characteristics of the aqueous automatic dishwashing detergent are formed by the incorporation into the aqueous liquid automatic dishwashing detergent of a mixture of at least one alkali metal silicate and at least one inorganic or organic compound containing an alkali metal cation in the critical weight ratio of from 1:1 to 100:1, preferably from 1:1 to 35:1, and more preferably from 1:1 to 20:1.

The electrolyte thickening molecules must be used in very concentrated (approaching saturation) aqueous solutions. Concentrations vary for each type of molecule used to thicken the silicate, since the solubility varies from molecule to molecule. For a given quantity of electrolyte solution thickening increases with the concentration of the solution.

Alkali Metal Compound

The composition must contain an inorganic or organic compound having an alkali metal cation. These can be typical detergent builder salts. The detergent

builder salts of the instant invention are selected from the group consisting of sodium, lithium and potassium carbonate; lithium, sodium and potassium bicarbonate; sodium, lithium and potassium sesquicarbonates; sodium, lithium and potassium orthophosphates, tripolyphosphates (hydrated or anhydrous), pyrophosphates, metaphosphates and hexametaphosphates; tetrasodium or tetrapotassium pyrophosphates; trisodium or tripotassium orthophosphate; sodium, lithium and potassium tetraborate anhydrous, pentahydrate and decahydrate; alkali metal phosphinates, and mixtures thereof, as illustrative of the inorganics; and nitrilotriacetate, sodium polymaleate, sodium and potassium salts of ethylene diamine tetraacetic acid, and the like, and mixtures thereof, as illustrative of the organics.

A preferred solid builder salt is an alkali metal polyphosphate such as sodium tripolyphosphate ("NaTPP") or potassium tripolyphosphate ("KTPP"). In place of all or part of the alkali metal polyphosphate one or more other detergent builder salts can be used. Suitable other alkali metal organic or inorganic compounds are alkali metal citrates, borates, lower polycarboxylic acid salts, polyacetates, tartrates, maleates, alkenyl succinates, carboxymethyloxy succinates, nitrilotriacetates, polyacrylates, polymaleic anhydrides and copolymers of polyacrylates and polymaleic citrates anhydrides and polyacetal carboxylates.

Additionally, the organic compound could be an anionic surfactant containing an alkali metal cation as subsequently set forth herein. Other suitable inorganic compounds containing an alkali metal cation are sodium, potassium and lithium chlorides; sodium, potassium and lithium sulfates; and sodium, potassium and lithium nitrates. The weight ratio of the alkali metal silicate to the inorganic or organic compound containing the alkali metal cation is 1:1 to 100:1, more preferably 1:1 to 20:1.

The phosphate builders, where not precluded due to local regulations, are preferred, and mixtures of tetrapotassium pyrophosphate (TKPP) and sodium tripolyphosphate (NaTPP) (especially the hexahydrate) may be used. Typical builders also include those disclosed in U.S. Patent Nos. 4,316,812, 4,264,466 and 3,630,929

and those disclosed in U.S. Patent Nos. 4,144,226, 4,135,092 and 4,146,495, all of which are herein incorporated by reference.

The inorganic or organic compound containing an alkali metal compound can additionally be an anionic surfactant containing an alkali metal cation as set forth below. Other suitable inorganic compounds containing an alkali metal cation are sodium, potassium and lithium halides (e.g., chlorides); sodium, potassium and lithium sulfates; sodium, potassium and lithium nitrates; and mixtures thereof. The weight ratio of the alkali metal silicate to the inorganic or organic compound containing the alkali metal cation is from 1:1 to 100:1, preferably from 1:1 to 20:1.

Bleach

Although any chlorine bleach compound may be employed in the compositions of this invention, such as dichloro-isocyanurate, 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 a sufficient amount of at least one chlorine bleach compound to provide from 0.2 to 4.0% by weight of available chlorine, as determined, for example, by acidification of 100 parts of the composition with excess hydrochloric acid. A solution containing from 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.

The at least one halogen containing compound can be selected from various halogen bleaches. Examples of such bleaches include those selected from the group consisting essentially of the alkali metal and alkaline earth salts of hypohalite, haloamines, haloimines, haloimides and haloamides. All of these are believe to produce hypohalous bleaching species in situ. Hypochlorite and compounds producing hypochlorite in aqueous solution are preferred, although hypobromite is

also suitable. Representative hypochlorite-producing compounds include sodium, potassium, lithium and calcium hypochlorite, chlorinate trisodium phosphate dodecahydrate, potassium and sodium dichloroisocyanurate and trichlorocyanuric acid. Organic bleach sources suitable for use include deterocyclic N-bromo and N-chloro imides such as tri-chlorocyanuric and tribromocyanuric acid, dibromo- and dichlorocyanuric acid, and potassium and sodium salts thereof, N-brominated and N-chlorinated succinimide, malonimide, phthalimide and naphthalimide. Also suitable are hydantions, such as dibromo- and dichloro dimethylhydantion, chlorobromodimethyl hydantoin, N-chlorosulfamide (haloamide) and chloramine (haloamine). Particularly preferred in this invention is sodium hypochlorite having the chemical formula NaOC1, in an amount ranging from 0.1% to 15%, more preferably from 0.2% to 10% and most preferably from 1.0% to 6.0%. This bleach is an oxidizing cleaning agent which is very effective against oxidizable stains.

Surfactants

Many organic functional groups present in surfactant molecules are oxidized by bleaches such as sodium hypochlorite. These groups include primary or secondary hydroxyl groups (Milton J. Rosen and Zhen Huo Zhu, JAOCS, Volume 69, No. 7, July 1992, pages 667-671). Although the types of surfactants that may be used in bleach-containing compositions are limited, surfactants may be chosen from the conventionally-used bleach stable surfactants including alkanesulfonates or alkylarenesulfonates, including anionics such as the alkyl benzene sulfonates and sulfates, the alkyl sulfonates and sulfates, alcohol sulfonates and sulfates, the alcohol ether sulfonates and sulfates, the alkyl ether sulfonates and sulfates, olefin sulfonates and sulfates, paraffin sulfonates and sulfates, fatty acid monoglyceride sulfonates and sulfates.

The preferred anionic sufactants are the paraffin sulfonates (C_{10}-C_{20}); the linear alkyl benzene sulfonates, the alcohol and the alcohol ether sulfates. Particularly preferred surfactants herein 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 3B-2 (sodium n-decyl diphenyloxide disulfonate) and DOWFAX 2A-1.

The most preferred anionics (non-soap) are the C_{12}-C_{18} paraffin sulfonates in the form of their alkali metal salts; C_8-C_{20} alkyl benzene sulfonates with C_{12}-C_{16} being highly preferred; the alkyl sulfates of C_{12}-C_{18} and the corresponding ether sulfates with 3 to 50 (e.g., 3, 5, 10, 20, 30 and 50) moles of condensed ethylene oxide. The most preferred salt forming cation is sodium. The amount of the anionic may range from 0 to 15% by weight, preferably from 1 to 10% by weight and more preferably from 1 to 5% by weight.

Some specific examples of suitable anionics are sodium lauryl sulfate, sodium paraffin (C_{14}-C_{17}) sulfonate, sodium decyl sulfate, socium tridecyl sulfonate, sodium tallow alkyl sulfate, sodium coconut alkyl sulfate, sodium oxotridecyl-triethoxyl sulfate, sodium dodecyl benzene sulfonate, sodium tridecyl benzene sulfonate, sodium tetradecyl benzene sulfonate and sodium (C_{15}) olefin sulfonate.

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.

Detergent active material useful herein should be stable in the presence of chlorine bleach, especially hypochlorite bleach, and for this purpose those of the organic anionic, amine oxide, phosphone oxide, sulphoxide or betaine water dispersible surfactant types are preferred, the first mentioned anionics being most preferred. Particularly preferred surfactants herein 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 3B-2 (sodium n-decyl diphenyloxide disulfonate) 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 sodium benzoate, the primary alkylsulphates, alkylsulphonates, alkylarylsulphonates and sec.-alkylsulphates. Examples include sodium C_{10}-C_{18}

alkylsulphates such as sodium dodecylsulphate and sodium tallow alcoholsulphate; sodium C_{10}-C_{18} alkanesulphonates such as sodium hexadecyl-1-sulphonate and sodium C_{12}-C_{18} alkylbenzenesulphonates such as sodium C_{10}-C_{18} alkanesulphonates such as sodium hexadecyl-1-sulphonate and sodium C_{12}-C_{18} 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 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, myristyl-dimethylamine 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.

Another useful surfactant in the instant dilatant prespotter cleaning compositions is Neodol 25-3S is made by Shell Chemical Company, Inc. This surfactant is a condensation product of a mixture of a higher fatty alcohols averaging 12 to 13 carbon atoms and ethylene oxide groups being present at an average number of 6.5. Neodol 25-3S is terminated by sulfate groups, and is bleach-compatible. The higher alcohols are primary alkanols.

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 be used.

The liquid nonionic surfactants that can be, optionally, used in the present aqueous liquid automatic dishwasher detergent compositions are well known. A wide variety of these surfactants can be used. The nonionic synthetic organic detergents are generally described as ethoxylated propoxylated fatty alcohols which are low-foaming surfactants and are possibly capped, characterized by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic or alkyl aromatic hydrophobic compound with ethylene oxide and/or propylene oxide. Practically any hydrophobic compound having a carboxyl, hydroxy and amido or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a nonionic detergent. The length of the hydrophilic or polyoxy ethylene propylene chain can be readily adjusted to achieve the desired balance between the hydrophobic and hydrophilic groups. Typical suitable nonionic surfactants are those disclosed in U.S. Patent Nos. 4,316,812 and 3,630,929.

Preferably, the nonionic detergents that are used are the low foaming poly-lower alkoxylated lipophiles, wherein the desired hydrophile-lipophile balance is obtained from addition of a hydrophilic poly-lower alkoxy group to a lipophilic moiety. A preferred class of the nonionic detergent employed is the poly-lower alkoxylated higher alkanol wherein the alkanol is of 9 to 18 carbon atoms and wherein the number of moles of lower alkylene oxide (of 2 or 3 carbon atoms) is from 3 to 15. Of such materials it is preferred to employ those wherein the higher alkanol is a high fatty alcohol of 9 to 11 or 12 to 15 carbon atoms and which contain from 5 to 8 or 5 to 9 lower alkoxy groups per mole. Preferably, the lower alkoxy is ethoxy but in some instances, it may be desirably mixed with propoxy, the latter, if present, usually being the minor (no more than 50%) portion. Exemplary of such compounds are those

wherein the alkanol is of 12 to 15 carbon atoms and which contain 7 ethylene oxide groups per mole.

Useful nonionics are represented by the low foaming Plurafac series from BASF Chemical Company which are the reaction product of a higher linear alcohol and a mixture of ethylene and propylene oxides, containing a mixed chain of ethylene oxide and propylene oxide, terminated by a hydroxyl group. Examples include a C_{13}-C_{15} fatty alcohol condensed with 6 moles ethylene oxide and 3 moles propylene oxide, a C_{13}-C_{15} fatty alcohol condensed with 7 mole propylene oxide and 4 mole ethylene oxide, and a C_{13}-C_{15} fatty alcohol condensed with 5 moles propylene oxide and 10 moles ethylene oxide. A particularly good surfactant is Plurafac 132 which is a capped nonionic surfactant. Another group of low foam liquid nonionics are available from Shell Chemical Company, Inc. under the Dobanol trademark: Dobanol 91-5, an ethoxylated C_9-C_{11} fatty alcohol with an average of 5 moles ethylene oxide, and Dobanol 25-7, an ethoxylated C_{12}-C_{15} fatty alcohol with an average of 7 moles ethylene oxide.

Other liquid nonionic surfactants that can be used are sold under tradename Lutensol SC 9713, Synperonic LF D25 or LF RA 30, Synperonic RA 30, Synperonic RA 40 and Synperonic RA 340. The Synperonic surfactants are especially preferred because they are biodegradable and low foaming.

Other useful surfactants are Neodol 25-7 and Neodol 23-6.5, made by Shell Chemical Company, Inc., which are condensation products of a mixture of higher fatty alcohols (primary alkanols) averaging 12 to 13 carbon atoms and the number of ethylene oxide groups present averages 6.5. Other examples of such detergents include Tergitol 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxylates made by Union Carbide Corp. The former is a mixed ethoxylation product of an 11 to 15 carbon atoms linear secondary alkanol with seven moles of ethylene oxide and the latter is a similar product but with nine moles of ethylene oxide being reacted. Another useful surfactant is Tergitol MDS-42 a mixed alkoxylation

product of 13-15 cations and alcohols with 10 moles of ethylene oxide and 5 moles of propylene oxide.

Also useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14 to 15 carbon atoms and the number of ethylene oxide groups per mole being 11.

In the preferred poly-lower alkoxylated higher alkanols, to obtain the best balance of hydrophilic and lipophilic moieties the number of lower alkoxies will usually be from 40% to 100% of the number of carbon atoms in the higher alcohol, preferably from 40 to 60% thereof and the nonionic detergent will preferably contain at least 50% of such preferred poly-lower alkoxy higher alkanol.

Also useful are the alkylpolysaccharide surfactants, which are used alone or in conjunction with the aforementioned surfactants and have a hydrophobic group containing from 8 to 20 carbon atoms, preferably from 10 to 16 carbon atoms, most preferably from 12 to 14 carbon atoms, and polysaccharide hydrophilic group containing from 1.5 to 10, preferably from 1.5 to 4, more preferably from 1.6 to 2.7 saccharide units (e.g., galactoside, glucoside, fructoside, glucosyl, fructosyl; and/or galactosyl units). Mixtures of saccharide moieties may be used in alkyl polysaccharide surfactants. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkoxide chain can contain up to 30, preferably less than 10, most preferably 0, alkoxide moieties. Suitable alkylpolysaccharides are decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, and octadecyl, di-, tri-, tetra-, penta- and hexaglucosides, galactosides, lactosides, fructosides, fructosyls, lactosyls, glucosyls and/or galactosyls and mixtures thereof.

The alkylmonosaccharides are relatively less soluble in water than the higher alkylpolysaccharides. When used in admixture with alkylpolysaccharides, the alkylmonosaccharides are solubilized to some extent. The use of

alkylmonosaccharides in admixture with alkylpolysaccharides is preferred. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexaglucosides.

The preferred alkyl polysaccharides are alkyl polyglucosides having the formula

$$R_2O(C_nH_{2n}O)_r(Z)_x$$

wherein Z is derived from glucose, R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl, hydroxyalkylphenyl, and mixtures thereof in which said alkyl groups contain from 10 to 18, preferably from 12 to 14 carbon atoms; n is 2 or 3 preferably 2, r is from 0 to 10, preferably 0; and x is from 1.5 to 8, preferably from 1.5 to 4, most preferably from 1.6 to 2.7. To prepare these compounds a long chain alcohol (R_2OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkylpolyglucosides can be prepared by a two step procedure in which a short chain alcohol (R_1OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkylpolyglucosides can be prepared by a two step procedure in which a short chain alcohol (C_{1-6}) is reacted with glucose or a polyglucoside (x=2 to 4) to yield a short chain alkyl glucoside (x=1 to 4) which can in turn be reacted with a longer chain alcohol (R_2OH) to displace the short chain alcohol and obtain the desired alkylpolyglucoside. If this two step procedure is used, the short chain alkylglucoside content of the final alkylpolyglucoside material should be less than 50%, preferably less than 10%, more preferably less than 5%, most preferably 0% of the alkylpolyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkylpolysaccharide surfactant is preferably less than 2%, more preferably less than 0.5% by weight of the total of the alkylpolysaccharide. For some uses it is desirable to have the alkylmonosaccharide content less than 10%.

The used herein, "alkylpolysaccharide surfactant" is intended to represent both the preferred glucose and galactose derived surfactants and the less preferred

alkylpolysaccharide surfactants. Throughout this specification, "alkylpolyglucoside" is used to include alkylpolyglycosides because the stereochemistry of the saccharide moiety is changed during the preparation reaction.

An especially preferred APG glycoside surfactant is APG 625 glycoside manufactured by the Emery division of Henkel Corporation. APG 625 is a nonionic alkyl polyglycoside characterized by the formula:

$$C_nH_{2n+1}O(C_6H_{10}O_5)_xH$$

wherein n=10 (2%); n=12 (65%); n=14 (21-28%); n=16 (4-8%) and n=18 (0.5%) and x (degree of polymerization) = 1.6. APG 625 has: a pH of 6-8 (10% of APG 625 in distilled water); a specific gravity at 25°C of 1.1 g/ml; a density at 25°C of 9.1 lbs/gallon; a calculated HLB of 12.1 and a Brookfield viscosity at 35°C, 21 spindle, 5-10 RPM of 3,000 to 7,000 cps.

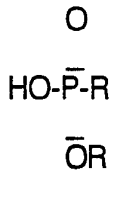
Mixtures of two or more of the liquid nonionic surfactants can be used and in some cases advantages can be obtained by the use of such mixtures.

The chlorine bleach stable, water dispersible organic detergent-active material (surfactant) will normally be present in the composition in minor amounts, generally 1% by weight of the composition, although smaller or larger amounts, such as from 0.1 to 5%, preferably from 0.3 to 0.4 to 2% by weight of the composition, may be used.

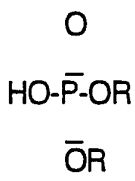
Foam Depressants

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 or KTPP which has a water softening effect, may aid in providing a degree of foam inhibition.

Optionally, at least one chlorine bleach stable foam depressant or inhibitor can be included. Particularly effective are the alkyl phosphoric acid esters of the formula



and especially the alkyl acid phosphate esters of the formula



In the above formulas, one or both R groups in each type of ester may represent independently a C_{12}-C_{20} alkyl or an alkoxylated, such as ethoxylated, 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 from 2 to 6 moles, more preferably from 3 to 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 di-esters 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. Other defoamers which may be used include, for example, the known silicones, such as are available from Dow Chemicals. When employed, proportions of from 0.05 to 1.5 weight percent, preferably from 0.1 to 0.5 weight percent, of foam depressant in the composition are typical. The weight ratio of detergent active component to foam depressant generally ranges from 10:1 to 1:1 and preferably from 5:1 to 1:1.

The fatty acid component may be any fatty acid having a carbon chain of from C_6-C_{30} with C_8-C_{20} being preferred. Most preferred are C_{10}-C_{18} and typically,

naturally occurring materials, such as coconut oil, palm oil, kernel oil, and animal tallow, serve admirably as sources for the fatty acids. A particularly preferred range of fatty acids is

C_{12}-C_{18} as one would find in coconut oil. A typical coconut oil fatty acid composition contains 50% C_{12}; 20% C_{14}; 8.5% C_{16}; and 10% C_{18} the balance other acid and even perhaps some neutral material, and is a liquid at 40C. While the most convenient sources are natural oils or fats yeilded, mixed acids, of course, the individual specific acids, and indeed any mixture of any number and chain length of acids within the parameter of C_6-C_{30} may be used. The soaps used are the alkali metal and ammonium salts with sodium and potassium preferred. The fatty acid may comprise from 0 to 15% by weight and preferably 0.5 to 10% anmd, more preferably 1 to 7% of the composition.

The abrasive employed inthe invention may be inorganic or polymeric. The inorganic abrasives are selected from the group consisting of quartz, pumice, samicite, titanium dioxide, aluminum oxide, silica sand, feldspar, silicon carbide and the like and mixtures thereof. The inorganic abrasives can be used along or in combination with polymeric abrasives. The inorganic abrasives which have a Mohr hardness of less than 3, more preferably less than 2.75 and are employed in the composition at 0 weight percent to 10 weight percent, more preferably 1 to 7.

The polymeric abrasive may be any material derived from a polymerizable composition, such as polyethylene, polypropylene, polystyrene, polyester, polyvinyl chloride, polyvinyl acetate, polymethyl methacrylate and various copolymers and interpolymers of the foregoing. The criteria for suitability are that the material does not scratch polymethyl methyacrylate and that the average particle size ranges from 10 to 150 microns and preferably from 25 to 100 microns and most preferably from 30 to 75 microns, e.g. 60 microns. For optimum performance it is most desirable to utilize a polyvinyl chloride abrasive powder whose average particle size is 60 microns, with a major amount being within the range of 30 to 75 microns. The molecular weight ranges of the polymeric abrasives may vary widely just so long as the physical

properties set out above are met. Generally, molecular weights will range from several thousand (e.g. 125,000; 5,000; 20,000) to several hundred thousand (e.g. 125,000; 250,000; 400,000) and upwards of several million (e.g. 1,000,000; 2,000,000; 4,000,000; 6,000,000). The amount of abrasive may range from 2% to 30% or more (e.g. 40%; 50%). A preferred range in the preferred formulations is from 5% to 25% and more preferred is a range of 5 to 15%, such as 7%; 10%; or 12%.

A large variety of optional ingredients may be included in the formulations of this invention. Optional additives include a hydrocarbon material, particularly a terpene, such as d-limonene. Such terpenes are readily available in many perfume materials which are generally added to most consumer cleaning products. The amount of the hydrocarbon may vary from 0.05 to 5% and preferably from 0.1 to 2 to 3%. Other additives which may be used include bleaches (liquid and solid hypochlorites, available, e.g. as NaOC1 solution or calcium hypochlorite powder; chloramines, chlorinated di- and trisodium phosphates, sodium and potassium dichlorisocyanurate, trichlorocyanuric acid, and so forth); buffers, caustic soda; caustic potash; suds boosters; enzymes; preservatives; disinfectants; colorants; fragrances and the like, may be used where desired and compatible. Generally, minor amounts of such auziliary materials are employed, e.g. 0.01 to 10% and often 0.1 to 5%.

The scouring compositions of this invention are alkaline and generally have a pH from 10 to 13. It is generally preferred to add in the formulations the fatty acid in free acid form and neutralize in situ with caustic soda (NaOH) or caustic potash (KOH), at the same time adjusting the pH to the desired level. A typical, preferred pH 11±0.5.

The organic compound, having at least one hydroxyl group which is employed in the instant scouring or paste compositions has the formula

$$C_nH_{2n+2-x}(OH)x$$

wherein x=1, 2 or 3 and n is 1 to 20, preferably 1 to 12. Typical examples of organic compounds having at least one hydroxyl group are selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, propylene glycol, 1,6-hexand-diol, sec-butanol, n-pentanol, esopentanol, neopentanol, n-

hexanol, isohexanol, n-heptanol, isooheptanol, n-octanol, eso-octanol, glycerol, butanidol, pentanediol, hexanetriol, hexanedecanol and pentadecanol. The concentration of the organic or inorganic compound containing the alkali metal cation or the organic compound continuing at least one hydroxyl group in the composition is .01 to 40 weight percent, more preferably 0.5 to 35 weight percent. The weight ratio of the alkali metal silicate to the inorganic or organic compound containing the alkali meta cation is 1000:1 to 1:1, more preferably 100:1 to 1:1 and most preferably 75:1 to 1:1. The weight rate of the alkali metal silicate to the organic compound continuing at least one hydroxyl group is 1000:1 to 1:1, more preferably 500:1 to 1:1. The resultant composition of the alkali metal silicate, water and the inorganic compound containing the alkali metal cation exhibits shear thickening characteristics. The viscosity of the resultant compositions at 10 $2s^{-1}$ at room temperature is 12 to 80 pascal seconds and the viscosity at room temperature at $5s^{-1}$ is 15 to 90 pascal seconds.

In addition to the silicate surfactant, optionally, a foam inhibitor, and the organic or inorganic compound having an alkali metal cation which compound can be the 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 from 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 pH in the wash bath of at least 9, preferably at least 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. potassium tripolyphosphate. Alkalinity can be achieved also by the buffering capability of the silicate. However, it is possible 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 0 to 8%, preferably

from 0.1 to 6%, more preferably from .5 to 4%, by weight of the composition will be sufficient to ensure the desired pH level.

Other conventional ingredients may be included in these compositions in small amounts, generally less than 3 weight percent, such as perfumes, 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 stale 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 manner of formulating the invention compositions may be critical. The order of mixing the ingredients as well as the manner in which the mixing is performed generally will have some effect on the dilatant properties of the composition, and in particular on product density (by 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 mixing the aqueous alkali metal silicate and an aqueous solution of alkali metal cation such as contained in an alkali metal detergent builder salt with stirring at a temperature of 15 to 30°C, more preferably from 20 to 25°C for 1 to 5 minutes. Saturated or near saturated salt solutions are preferred. Subsequently, after homogeneous mixing of the aqueous alkali metal silicate, and the inorganic or organic compound containing the alkali metal cation has been achieved, the hydroxide, surfactant, chlorine bleach and any previously unused alkali metal compound are added with stirring. It is preferred to add the optional foam depressant last. All of the additional ingredients can be added simultaneously or sequentially. Preferably, the ingredients are added 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 relatively moderate to medium shear rates to achieve complete and uniform mixing. Water may be added as the last ingredient to control viscosity. Mixing may be carried out at room temperature. The composition may be allowed to age for a few hours, if necessary, to cause dissolved or dispersed air to dissipate out of the composition.

The resultant composition of the alkali metal silicate and the inorganic compound containing the alkali metal cation exhibits shear thickening characteristics. The viscosity of the resultant compositions for a shear rate of 2 sec-1 at room temperature is 12 to 100 pascal seconds, more preferably 15 to 80 pascal seconds. When the viscosity is plotted against the shear rate for the compositions of the instant invention a positive slope is obtained thereby indicating that the instant compositions are shear thickening. Upon the application of increasing shear rate to an aqueous solution of the composition the aqueous solution will shear thicken and an increase in viscosity will occur. The compositions of the prior art exhibit a negative slope thereby showing these compositions are shear thinning - decrease in viscosity.

When the viscosity of the resultant composition is plotted against the shear rate for the compositions of the instant invention a positive slope is obtained thereby indicating that the instant compositions are shear thickening. Upon the application of increasing shear rate to an aqueous solution of the composition the aqueous solution will shear thicken and an increase in viscosity will occur. The compositions of the prior art exhibit a negative slope thereby showing these compositions are shear thinning (i.e., the prior art compositions exhibit a decrease in viscosity with increasing shear rate).

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. The shear thickening compositions can be readily poured from their containers 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. The compositions 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 liquid aqueous dilatant 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 following examples are provided to illustrate the present invention without being deemed limitative thereof. In all of the examples, all ingredient values are in weight % of active ingredient (a.i.)(i.e., net of aqueous solution).

Example 1:

The following formulations were prepared:

	A	B	C	D	E	F	G	H	I
Potassium Silicate $K_2O(2.1SiO_2)$ (39.2% a.i. in aq. soln.)	34.4%	23.5%	37.1%	35.7%	22.5%	28.8%	31.6%	30.9%	34.3%
Water	63.9	66.5	61.3	59.0	59.1	63.9	65.6	66.8	60.5
Sodium Chloride		10.0							
Lithium chloride	1.7						0.8	2.3	1.1
Potassium chloride			1.6						
Potassium tripolyphosphate					18.4				3.7
Sodium citrate				5.4					
Potassium carbonate						7.3			
NaOCL							2.0		
Anionic Surfactant (DOWFAX 3B2) obtained from Dow Chemical									0.4

Formulations A to D and G to I described above were tested with the following results (viscosity in Pascal seconds, RT at shear rates):

A	B	C	D	G	H	I
1 sec^{-1} 29Pa-s 2 30 5 34 7 38 12 43	2 sec^{-1} 88 Pa-s 5 104 7 123 10 153 12 182 15 195 17 205	7 sec^{-1} 2 Pa-s 10 3 12 3 15 4 17 5 20 6 25 7 30 8 35 10 40 11 43 11	1 sec^{-1} 13 Pa-s 2 12 5 13 7 14 10 14 12 15 15 16 17 17 20 20 22 21 23 21	2 sec^{-1} 30 Pa-s 5 32 7 34 8 38 10 43	.5 sec^{-1} 71 Pa-s .7 68 1 74 2 76 5 81 10 94 12 108 15 119	.5 sec^{-1} 228 Pa-s .7 222 1 224 5 261 7 328

Viscosity was measured under steady shear conditions on a Carri-Med CSL 100 rheometer, where radius = 2 or 4 cm. and angle = 4°. Cone and plate geometries were used. Viscosity was measured at a single shear rate value for 2 minutes. Samples, after loading on the instrument, were covered with a low viscosity oil on their exposed edges in order to prevent drying out. The data for Sample N from Example 2 obtained at a shear rate of $5s^{-1}$ is shown in Figure 1 and is representative of the materials.

Example 2

Formulations of the following ingredients were prepared as fully formulated liquid automatic dishwasher formulations:

	J	K	L	M	N
Potassium Silicate $K_2O(2.1SiO_2)$ (39.2% a.i. in aq. soln.)	22.5%	9.7%	26.7%	28.8%	
Sodium Silicate $Na_2O(3.25SiO_2)$ (39.2% a.i. in aq. soln.)		14.6			20.5
Water	57.7	64.9	61.6	62.0	55.6
Sodium polyacrylate*		3.0	3.2		
Dowfax 3B2	0.1	0.5	0.4	0.5	0.4
NaOH	0.1		0.2		0.2
Potassium Tripolyphosphate	18.4				17.7
Sodium Tripolyphosphates					4.4
NaOCl	1.2	1.3	1.3	1.4	1.2
Potassium carbonate		5.3	6.8	7.3	
Sodium carbonate		0.9			

* Sokolan PA-30 from BASF (sold as 45% a.i. in aq. soln.; MW=8,000; pH 7).

The following Brookfield data was obtained for three of the above samples:

Sample	RPM	Torque Reading	Factor	Viscosity (Pa-s)
L	0.5	0.6	160M	96
	1.0	1.5	80M	120
	2.5	3.9	32M	124.8
	5.0	8.2	16M	131.2
	10.0	21.9	8M	175.2
	20.0	62.4	4M	249.6

Sample	RPM	Torque Reading	Factor	Viscosity (Pa-s)
K	2.5	1.1	32M	35.2
	5.0	2.6	16M	41.6
	10	5.4	8M	43.2
	20	12.8	4M	51.2
	50	52.9 (2 min)	1.6M	84.6
	50	57.0 (4 min)	1.6M	91.2
	50	61.4 (6 min)	1.6M	98.2

Sample	RPM	Torque Reading	Factor	Viscosity (Pa-s)
J	2.5	0.8	32M	25.6
	5.0	1.7	16M	27.2
	10.0	3.7	8M	29.6
	20	7.9 (2 min)	4M	31.6
	20	8.6 (4 min)	4M	34.4
	20	8.8 (6 min)	4M	35.2
	50	27.6 (2 min)	1.6M	44.1
	50	29.3 (4 min)	1.6M	46.9

All readings were taken with the HATD Digital Brookfield Viscometer using Spindle #7 at room temperature (24°C).

Example 3

Formulation of the following ingredients were prepared according to the procedure of Example 1, wherein the sodium hypocholorite was added last to the mixed ingredients.

	A	B	C
Water	59.5%	58.5%	55.4
K2O(2.1)SiO2 Potassium silicate (39.2%)	36.3%	37.7%	36.3%
Neodol 25-3S	3.7%	3.8%	3.7%
NaOC1 (13%)	.5%		4.6%
Viscosity R.T. (pascal seconds) shear rate			
5 sec^{-1}	46 Pa-s		
7 sec^{-1}	53		
10 sec^{-1}	62		
12 sec^{-1}	88		
15 sec^{-1}	129		
20 sec^{-1}	183		

Example 4

Formulations of the following ingredients are prepared:

	A	B	C	D	E	F
Potassium Silicate 39.2%	38.9%	38.9%	38.9%	38.9%	38.8%	38.8%
Water	60.3%	60.3%	60.3%	60.3%	60.2%	60.2%
Methanol	.8%					
1-Propanol		.8%				
2-Propanol			.8%			
1-Heptanol				.8%		
Propylene Glycol					1.0%	
1.6 Hexanediol						1.0%
Viscosity RT (pascal seconds) at shear rate of						
2 sec^{-1}	28	36	34	4.0	11.4	65
5 sec^{-1}	30	37-38	35-36	4.1	12.2	70
7 sec^{-1}	32	39	38	4.3	12.8	76
10 sec^{-1}	34	42	41	4.9	13.5	--

To the solution of the aqueous potassium silicate is added with stirring at room temperature for 1-5 minutes the methanol, n-hexanol, 1-propanol, 2-propanol, 1-hetanol, propylene glycol and 1,6 hexanediol.

Example 5

Formulations of the following ingredients were prepared according to the procedure of Example 1, wherein the ingredients not sent forth in Example 1 are subsequently added to the mixed ingredients of Example 1 in the order as set forth in the following table.

	A
Potassium silicate (39.2%)	35.9%
Water	61.7%
Lithium Chloride	.9%
Dowfax 3B2	.4%
Silica Sand	1.1%
Viscosity, RT pascal seconds shear rate	
1 s^{-1}	4.6
2 s^{-1}	4.5
5 s^{-1}	4.4
7 s^{-1}	4.5
10 s^{-1}	4.6
12 s^{-1}	4.7
15 s^{-1}	4.8
17 s^{-1}	5.3
20 s^{-1}	5.5
25 s^{-1}	5.9
30 s^{-1}	6.6
35 s^{-1}	7.4
40 s^{-1}	8.8
45 s^{-1}	11.1

Example 6

The following formula was prepared:

	A
Potassium silicate (39.2%)	31.6%
Water	66.1%
Lithium chloride	2.3%

Viscosity poises, RT (pascal seconds)

.5 s^{-1}	71 Pa-s
.7 s^{-1}	68
1 s^{-1}	74
2 s^{-1}	76
5 s^{-1}	81
7 s^{-1}	71
10 s^{-1}	94
12 s^{-1}	108

To the solution of the aqueous potassium silicate was added with stirring at room temperature for 5 minutes the aqueous lithium chloride solution.

Example 7

The following paste formula was prepared:

Potassium silicate (39.2%)	34.3
Water	60.5
Lithium chloride	1.1
Dowfax 3B2	.4
Sodium tripolyphosphate	3.7

Viscosity (pascal seconds) shear rate

.5 s^{-1}	228 Pa-s
.7 s^{-1}	222
1 s^{-1}	224
5 s^{-1}	261
7 s^{-1}	328

To the solution of aqueous potassium silicate, and lithium chloride prepared according to the procedure of Example 1 was added at room temperature with moderate mixing the Dowfax 3B2 and the sodium tripolyphosphate.

WHAT IS CLAIMED IS:

1. A shear thickening composition having a viscosity at room temperature at 2 sec^{-1} of 12 to 100 pascal seconds which comprises by weight:

(a) 10 to 50% of an alkali metal silicate;

(b) 1 to 45% of an inorganic or organic compound having an alkali metal cation;

(c) 0 to 5.0% of at least one organic detergent active material; and

(d) water.

2. The composition of claim 1, wherein said alkali metal silicate is selected from the group consisting of lithium silicate, sodium silicate and potassium silicate.

3. The composition of claim 2, wherein said inorganic or organic compound is selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates, alkali metal hydroxides, alkali metal sulfates, alkali metal nitrates and alkali metal halides and mixtures thereof.

4. The composition of claim 1 further including at least inorganic or organic builder salt containing an alkali metal cation.

5. The composition of claim 7 further including a chlorine bleach compound.

6. A composition which comprises, on a weight of active ingredient (i.e., net of aqueous solution) basis:

(a) from 10 to 50% of at least one alkali metal silicate;

(b) from 0.1 to 50% of at least one inorganic or organic compound containing an alkali metal cation;

(c) from 0.1 to 15% of at least one halogen containing compound;

(d) from 0 to 15% of at least one detergent active material; and

(e) water,

wherein the composition thickens upon the application of shear.

7. The composition of claim 6, wherein said at least one alkali metal silicate is selected from the group consisting of lithium silicate, sodium silicate and potassium silicate.

8. The composition of claim 7, wherein said at least one inorganic or organic compound containing an alkali metal cation are selected from the group consisting of alkali metal orthophosphates, alkali metal pyrophosphates, alkali metal tripolyphosphates, alkali metal phosphinates, alkali metal carbonates, alkali metal citrates, alkali metal chlorides, alkali metal sulfates and sulfonates and alkali metal nitrates.

9. The composition of claim 8, wherein said at least one halogen containing compound comprises an alkali metal hypochlorite.

10. A shear thickening composition having a viscosity at room temperature at a 2 sec-1 of 10 to 100 pascal seconds which comprises approximately by weight:

(a) 5 to 50% of an alkali metal silicate;

(b) 0.1 to 15% of a surfactant having at least one sulfate group;

(c) 0.1 to 10% of a halogen containing compound; and

(d) the balance being water.

11. The composition of claim 10 wherein said alkali metal silicate is selected from the group consisting of lithium silicate, sodium silicate and potassium silicate and mixtures thereof.

12. The composition of claim 11 wherein said nonionic surfactant is an ethoxylated alcohol formed from higher fatty alcohols having 12 to 13 carbon atoms and 5 to 15 moles of ethylene oxide.

13. A shear thickening composition having a viscosity at room temperature at 2 sec^{-1} of 12 to 100 pascal seconds which comprises by weight:

(a) 5 to 50 of an alkali metal silicate;

(b) 0.1 to 50 of an inorganic or organic compound having an alkali metal cation or an organic compound containing at least one hydroxyl group;

(c) 0.1 to 10% of an abrasive; and

(d) water.

14. The composition of claim 13, wherein said alkali metal silicate is selected from the group consisting of lithium silicate, sodium silicate and potassium silicate.

15. The composition of claim 14, wherein said inorganic or organic compound is selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates, alkali metal hydroxides, alkali metal sulfates, alkali metal nitrates and alkali metal halides and mixtures thereof.

16. The composition of claim 15 further including a fatty acid or a metal salt of a fatty acid.

17. The composition of claim 16 further including at least one surfactant.

18. The composition of claim 17 wherein said abrasive is a polymeric or an inorganic abrasive.

19. A paste type composition having a viscosity at room temperature at a shear rate of 2 sec-1 of 12 to 80 pascal seconds and a viscosity at room temperature of 15 to 90 pascal seconds which comprises by weight percent of:

(a) 10 to 50% of an alkali metal silicate;

(b) 0.1 to 40% of an inorganic or organic compound having an alkali metal cation or an organic compound containing at least one hydroxyl group; and

(c) water.

20. The composition of claim 19, wherein said alkali metal silicate is selected from the group consisting of lithium silicate, sodium silicate and potassium silicate.

21. The composition of claim 20, wherein said inorganic or organic compound is selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates, alkali metal hydroxides, alkali metal sulfates, alkali metal nitrates and alkali metal halides and mixtures thereof.

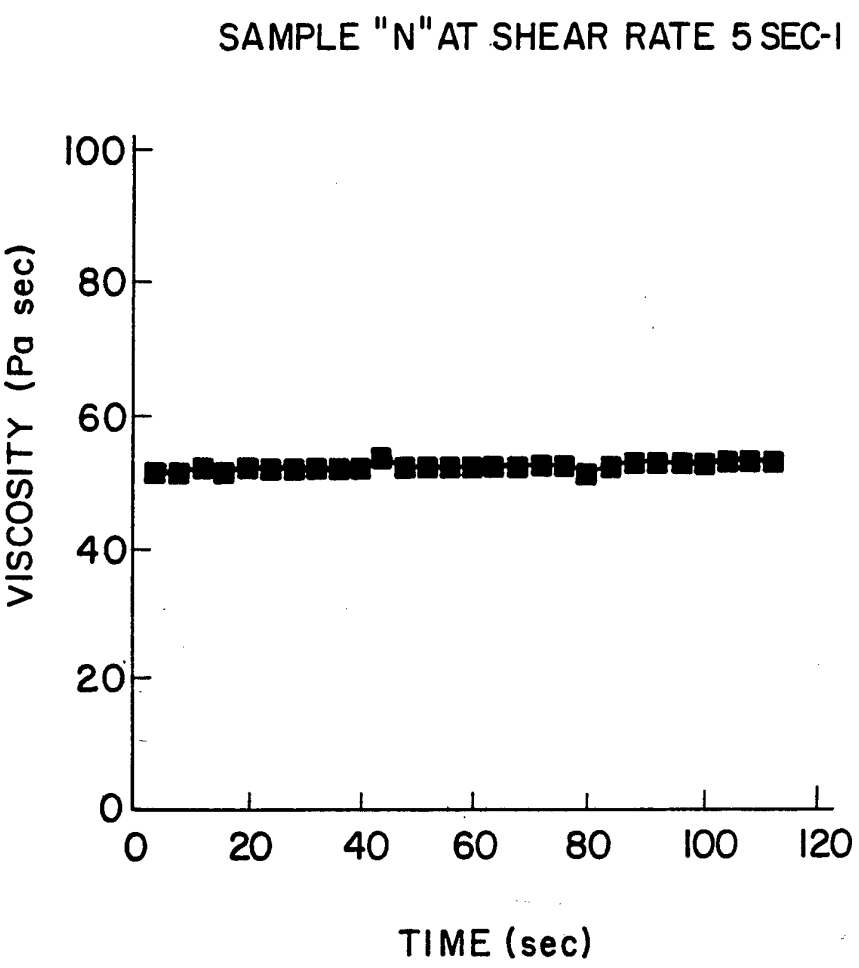

SAMPLE "N" AT SHEAR RATE 5 SEC-1
VISCOSITY (Pa sec)
100
80
60
40
20
0
0
20
40
60
80
100
120
TIME (sec)

FIG. 1

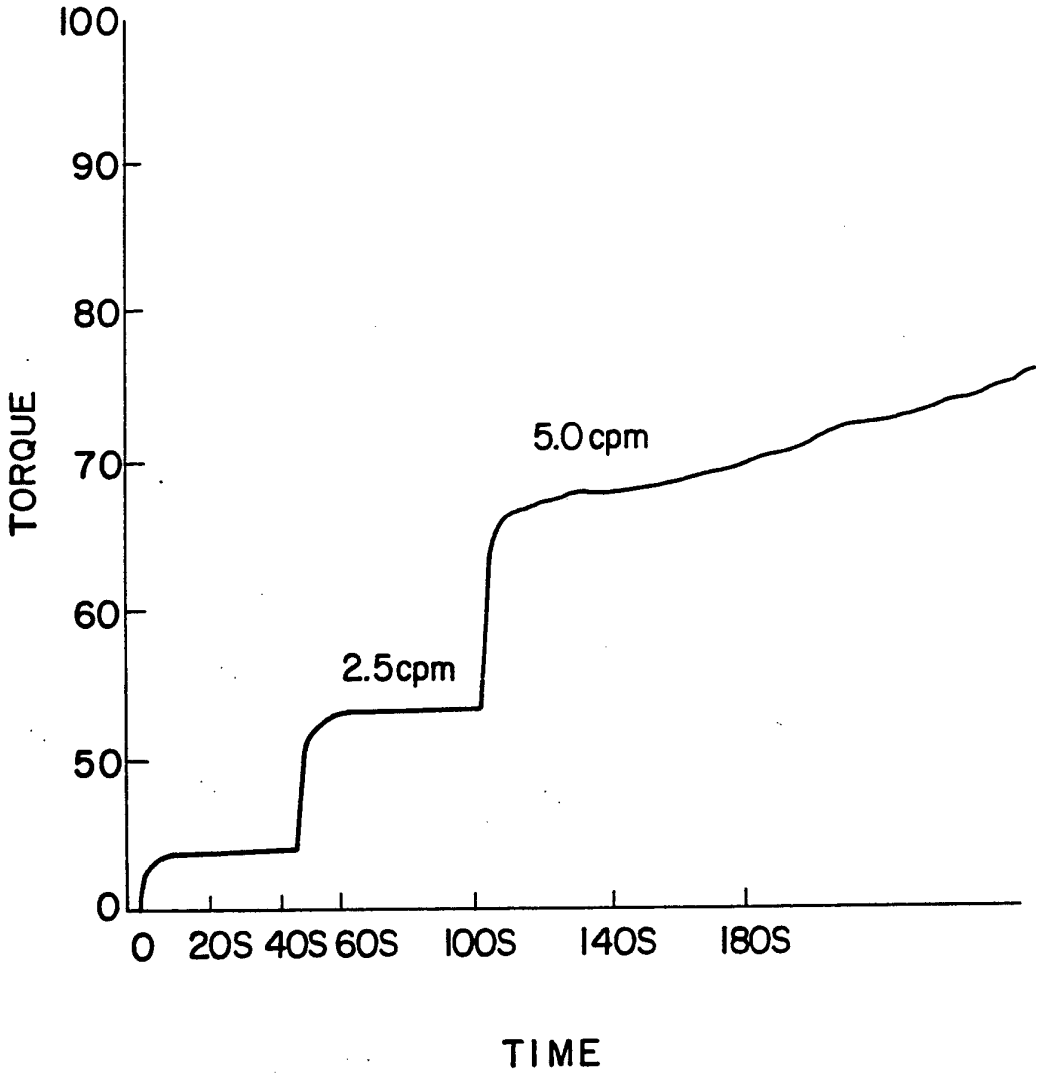

100
90
80
70
60
50
0
TORQUE
5.0 cpm
2.5cpm
0
20S
40S
60S
100S
140S
180S
TIME

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 93/07610

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C11D17/00 C11D3/08 C11D3/395

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 118 658 (HENKEL KGAA.) 19 September 1984 see page 3, line 22 - page 6, line 35 see page 9, line 1 - line 4; claims	1-9, 19-21
X	EP,A,0 331 370 (UNILEVER) 6 September 1989 see the whole document	1-9, 19-21
X	US,A,4 452 731 (WATANABE ET AL.) 5 June 1984	19-21
A	see column 3, line 44 - column 5, line 46; claims 1-7,19; example 47	1-3
A	EP,A,0 011 984 (S.C.JOHNSON & SON, INC.) 11 June 1980 see the whole document	1-18

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 January 1994	07. 02. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Serbetsoglou, A

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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 93/07610

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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1

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International Application No
PCT/US 93/07610

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