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(58) Field of search
C5D

(54) Detergent for automatic dishwasher

(57) A thixotropic aqueous detergent for use in household automatic dishwashers comprises a liquid phase which is water containing dissolved alkali metal tripolyphosphate and alkali metal silicate and dispersed non-swelling clay thickener and a solid phase which is mainly sodium tripolyphosphate. It contains a potassium compound, to give a K:Na weight ratio in the range of about 0.04 to 0.5. A process for making such slurries is also disclosed.

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FIG. I

EXAMPLE 4

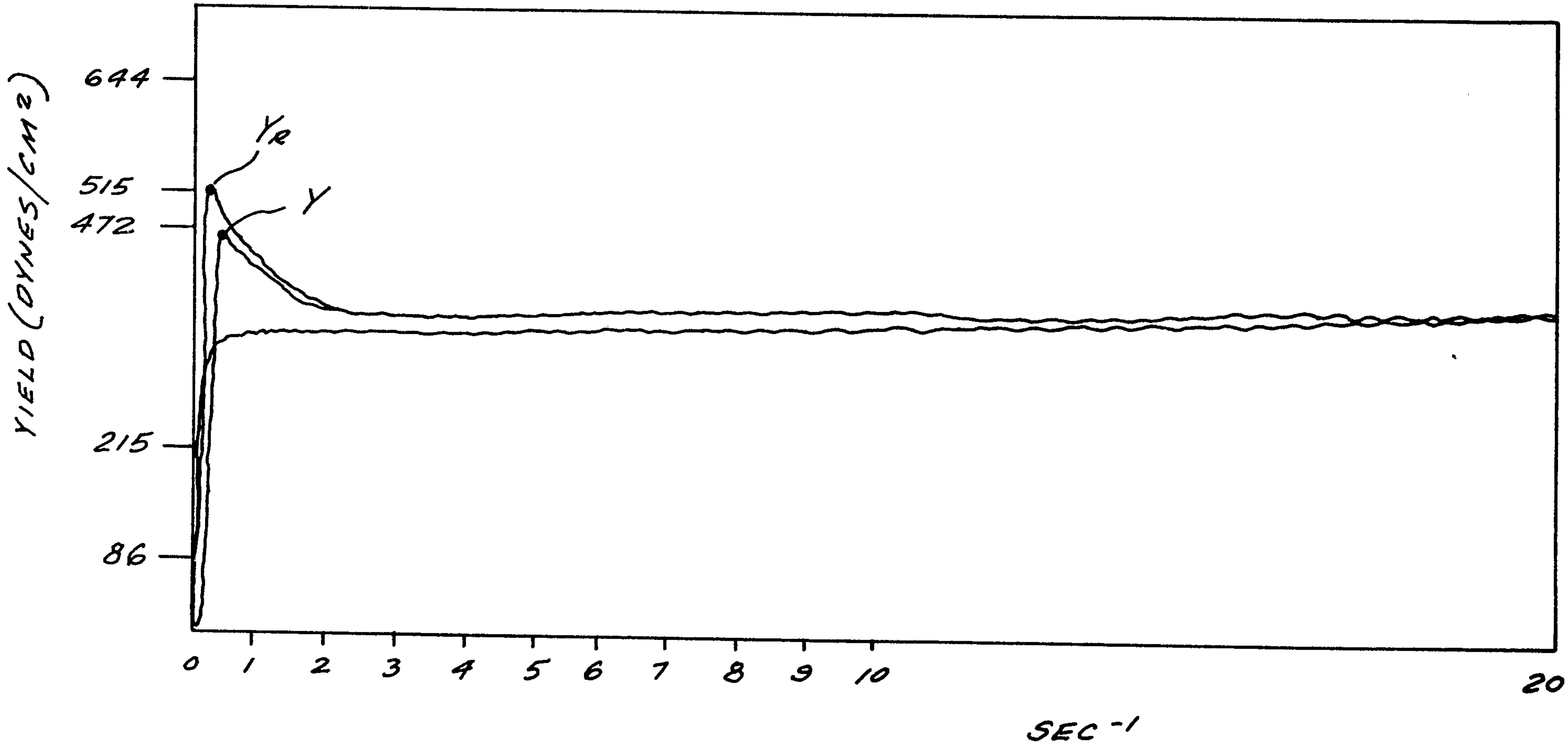


FIG. 2

EXAMPLE 5

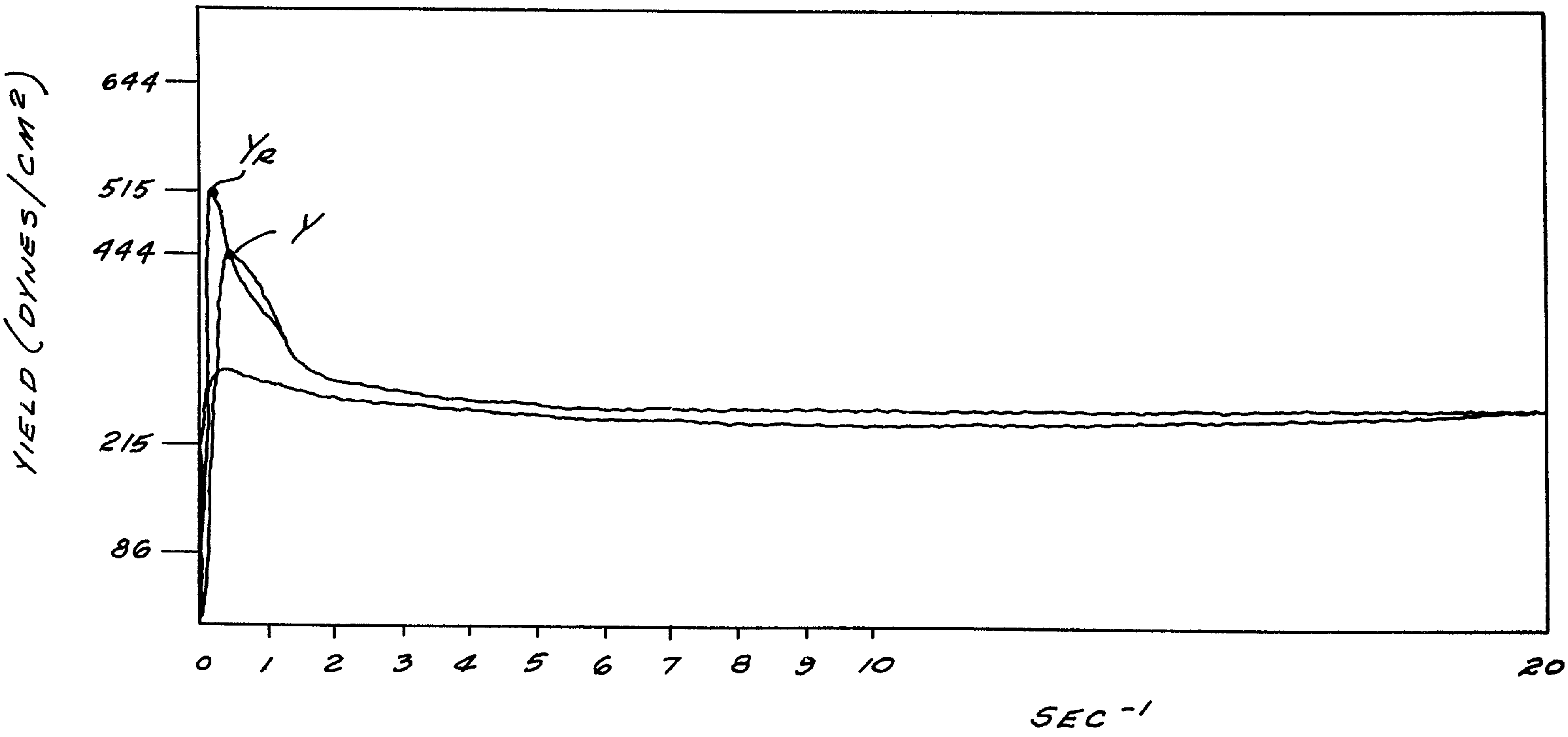
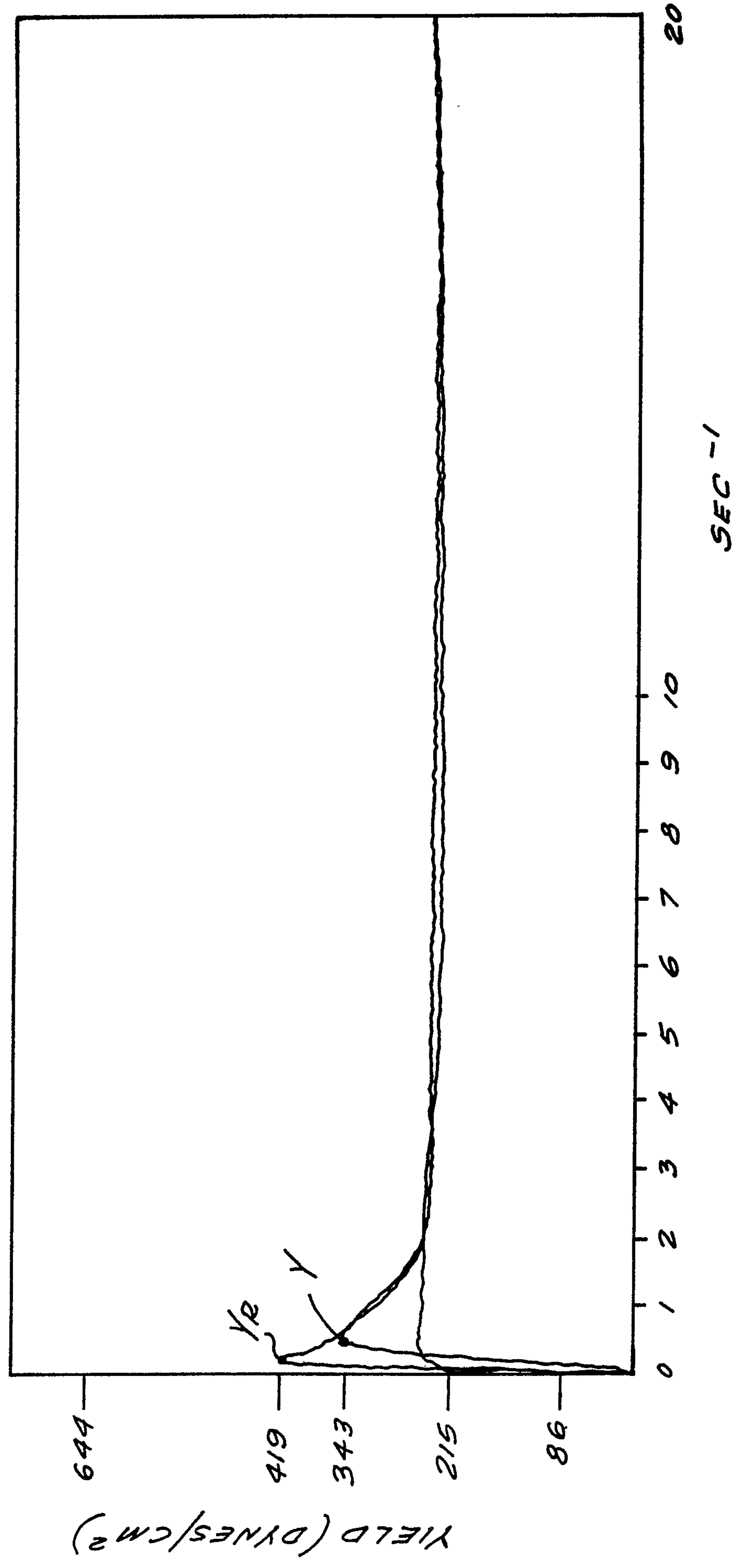


FIG. 3

EXAMPLE 6



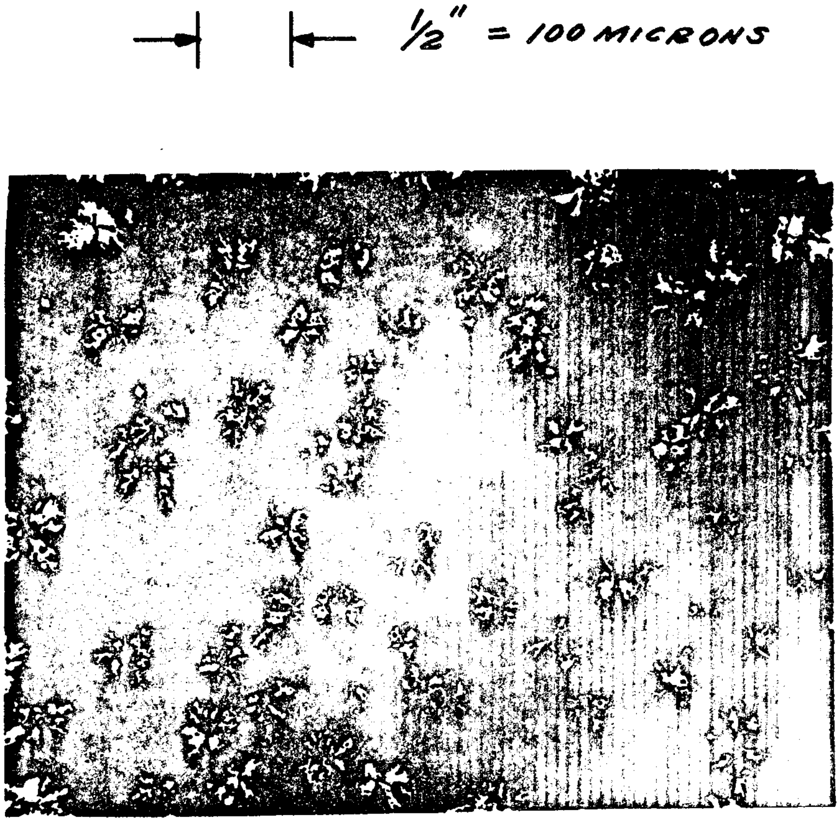


FIG. 4

SPECIFICATION

Process for making thixotropic detergent compositions

The present invention relates to an aqueous thixotropic automatic dishwasher detergent. One aspect of this invention relates to such a composition comprising a liquid phase which is water containing dissolved tripolyphosphate, silicate and alkali metal ions and a dispersed non-swelling clay thickener (preferably attapulgus clay) and a solid phase which is mainly sodium tripolyphosphate. The composition preferably also contains a chlorine bleach (advantageously dissolved sodium hypochlorite) and a bleach-resistant anionic surfactant. It also preferably contains an alkali metal carbonate.

It has now been found that greatly improved results are obtained by including a limited proportion of a water-soluble potassium compound, e.g. a potassium salt (or KOH), in the composition, to provide a K:Na weight ratio which is in the range of about 0.04 to 0.5, preferably 0.07 to 0.4 such as about 0.08 or about 0.15. The resulting product is much more stable in that it has less tendency to thicken undesirably or separate on ageing at, say, 100° F (38° C). Also, substitution of a portion of the sodium salt by the same weight of the corresponding potassium salt results in a considerable reduction in viscosity (e.g. as measured with a Brookfield HATD viscometer, at 25° C at 20 rpm using spindle #4) greater stability against separation on ageing (e.g. at room temperature), and inhibition of growth of relatively large crystals on storage. The reduction in viscosity makes for easier handling in the production plant, easier dispensing in use, and makes it easier for the consumer to destroy the thixotropic structure of the product (by shaking the container in which it is packaged) so that it can be poured readily into the detergent cup(s) of a household automatic washing machine.

This subject matter is claimed in our copending application, serial no. .... filed coterminously with the present application.

In the formulation of the product, the proportions and ingredients may be as follows; one preferred set of ranges of proportions is, approximately, by weight:

(a) 8. to 35% alkali metal tripolyphosphate,
(b) 2.5 to 20% sodium silicate,
(c) 0 to 9% alkali metal carbonate,
(d) 0.1 to 5% chlorine bleach stable, water-dispersible organic detergent active material,
(e) 0 to 5% chlorine bleach stable foam depressant,
(f) chlorine bleach compound in an amount to provide about 0.2 to 4% of available chlorine, and
(g) thixotropic thickener in an amount sufficient to provide the composition with a thixotropy index of about 2.5 to 10.

Preferably, in the compositions disclosed herein, the proportion of sodium tripolyphosphate is above 15% (more preferably in the range of about 20 to 25 or 30%), the proportion of sodium silicate is at least about 4% (such as in the range of about 5 to 10 or 15%), the proportions of alkali metal carbonate is about 2 to 6 or 7%, the proportion of chlorine bleach bleach is such as to provide above 0.5% available chlorine (e.g. about 1 to 2% available Cl), the proportion of detergent active material is in the range of 0.1 to 0.5%. Calculated as SiO_2, a preferred range of proportions of sodium silicate represents about 3.5 to 7% SiO_2 in the composition.

The proportion of water in the compositions (measured by "Cenco moisture analyzer", in which the sample is heated, by an infrared lamp, until it comes to constant weight) is preferably in the range of about 40-50%, more preferably about 43-48% such as about 44 or 46%.

The compositions disclosed herein usually have pH's well above 11 or 12. In one preferred type of formulation, the composition when diluted with water to 0.75% concentration has a pH in the range of about 10.7 to 11.3.

The compositions disclosed herein are preferably formulated to have viscosities (measured with a Brookfield HATD) viscometer at 25° C at 20 rpm using spindle #4) of less than about 8000 centipoises and more preferably in the range of about 2000 or 3000 to 7000 centipoises such as about 4000 to 6000 centipoises and preferably less than 6000 poise. The viscosity, and other properties, are preferably measured several days (e.g. a week) after the composition is prepared; it is good practice to shake the sample before measuring its viscosity and to let the viscometer run for some 90 seconds before taking the reading.

The compositions discosed herein have yield values well above 2000 dynes per cm^2 and are preferably formulated to have yield values of less than about 1100 dynes/cm^2 and more than about 300 dynes/cm^2, more preferably less than about 900 dynes/cm^2 such as about 400 to 600 dynes/cm^2. The yield value is an indication of the shear rate at which the thixotropic structure breaks down. It is measured with a Haake RV12 or RV100 rotational viscometer using spinde MVIP at 25° C with a shear rate rising linearly in 5 minutes (after a 5 minute rest period) from zero to 20 $sec.^{-1}$. In the Haake viscometer, a thin layer of the material is sheared between a rotating cylinder and the closely adjacent cylindrical wall of the surrounding container. Figures 1-3 are graphs obtained on such testing of the products of the three Examples indicated thereon, with the peaks Y showing the yield values.

Another factor measured with the aforesaid Haake viscometer is the degree to which the composition recovers its thixotropic structure. In one measuring technique after the 5 minute period of increasing shear rate mentioned above, the rotation is decelerated to zero over 5 minutes then after a 30 second rest period the rotation is again accelerated to raise the shear rate linearly in 5 minutes from zero to 22.6 $sec.^{-1}$. This gives a second yield value, i.e. peaks Y_r in Figure 1. Preferably this second (recovered) yield value is at least 200 dynes/cm^2, such as at least 50%, 75% or more of the initially measured yield value.

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 and representations in which:

Figures 1-3 are graphs obtained on viscosity testing (as described above) of the products of Examples 4, 5 and 6, respectively, with the peaks Y showing the yield values.

Figure 4 is a photomicrograph (taken on the scale indicated thereon) of the composition of Example 4.

In this application all proportions are by weight unless otherwise indicated. In the Examples atmospheric pressure is used unless otherwise indicated.

In these Examples, Attagel #50 is powdered attapulgite clay (from Engelhard Minerals & Chemicals, whose trade literature indicates that, as produced, it contains about 12 wt.% free moisture, as measured by heating at 220° F (104° C), and has a B.E.T. surface area of about 210 m^2/g calculated on a moisture-free basis); Graphtol Green is a colouring agent; LPKN 158 is an antifoam agent from American Hoechst (Knapsack) comprising a 2:1 mixture of mono- and di- (C_{16}-C_{18}) alkyl esters of phosphoric acid; the sodium silicate has an $Na_2O:SiO_2$ ratio of 1:2.4; Dowfax 3B2 is a 45% aqueous solution of Na mono- decyl/didecyl diophenyloxide disulphonates, a bleach-resistant anionic surfactant; STPP is sodium tripolyphosphate. Unless otherwise indicated, the STPP is added in the form of the finely powdered commercial anhydrous material whose water content is about 0.5%, in such material typically about 4.5-6.5% of the material is present as the pyrophosphate. The water used is deionized water unless otherwise indicated.

Example 1

The following ingredients are added to a vessel in the order given below while mixing with a conventional propeller-type laboratory stirrer. The temperatures and mixing times at various stages are also indicated below:

	mass(g)	temperature (°F/°C)	time (min.)
10% Graphtol green (colour)	5		
130°F water	1746		
molten LPKN 158 (antifoam)	8		
Dowfax 3B2 (surfactant)	40		
		126/52	2
9:1 mixture of Attagel #50 and TiO_2 white pigment	180		
		122/50	1
		120/49	3
soda ash (Na_2CO_3)	275		
K_2CO_3	75		
		134/57	1
		132/36	3
Finely powdered STPP hexahydrate	750		
		127/53	1
		125/52	3
		124/51	5
47.5% aqueous solution of sodium silicate premixed with	421		
50% aqeuous solution of NaOH	150		
		118/48	3
13% aqeuous solution of NaOCl	500		
		108/42	3
Finely powdered STPP hexahydrate	750	108/42	1
Total	5000g	107/42	5

The viscosity of the mixture, measured as indicated above, is about 5000 centipoises after ageing for 3 weeks at 100° F (38° C) and is about 4800 centipoises after 3 months ageing at 100° F (38° C).

In this Example, the STPP hexahydrate has the following approximate size distribution:

U.S.S. Sieve	microns	%
on #10	greater than 2000	0
on #40	greater than 420	0
on #100	greater than 149	25.4
on #200	greater than 74	31.5
on #325	greater than 44	16.5
through #325	less than 44	25.9

Examples 2a to 2e

Example 2a is a comparison example.

The following formulations given in Tables 1A and 1B are prepared and their properties are measured as indicated below:

The ingredients are mixed in the following order: water, colour, clay, one half of the phosphate, defoamer, hypochlorite, sodium carbonate, potassium carbonate, NaOH, silicate, second half of phosphate, surfactant.

TABLE 1A

	Proportions		
Examples	*2a*	*2b*	*2c*
Ingredients			
Clay (attagel 50)	3.285	3.285	3.285
STPP	23.0	23.0	17.01
Potassium tripolyphosphate	–	–	–
Potassium Pyrophosphate	–	–	5.99
Sodium Carbonate	5.0	–	5.0
Potassium Carbonate	–	5.0	–
Sodium Hypochlorite (12%)	9.375	9.375	9.375
Sodium Hydroxide (50%)	2.05	2.05	2.05
Sodium Silicate (47.5%)	10.53	10.53	10.53
Surfactant (Dowfax 3B–2)	0.80	0.80	0.80
Defoamer (Knapsack Lp Kn)	0.16	0.16	0.16
Colour	0.381	0.381	0.381
Water	Balance	Balance	Balance
Properties			
Capillary drainage time (min.)	8.2	12.1	10.9
Viscosity (cps) on 100° F (28° C) ageing			
for 1 week	9080	3100	2900
for 2 weeks	9200	3480	2820
for 3 weeks	9300	3600	3040

TABLE 1B

Examples	*2d*	*2e*
Ingredients		
Clay (attagel 50)	3.285	3.285
STPP	16.5	23.0
Potassium tripolyphosphate	6.5	–
Potassium Pyrophosphate	–	–
Sodium Carbonate	5.0	2.5
Potassium Carbonate	–	2.5
Sodium Hypochlorite (12%)	9.375	9.375
Sodium Hydroxide (50%)	2.05	2.05
Sodium Silicate (47.5%)	10.53	10.53
Surfacttant (Dowfax 3B–2)	0.80	0.80
Defoamer (Knapsack Lp Kn)	0.16	0.16
Colour	0.381	0.381
Water	Balance	Balance
Properties		
Capillary drainage time (min.)	11.4	11.2
Viscosity (cps) on 100° F (28° C) ageing		
for 1 week	5120	5400
for 2 weeks	6340	5240
for 3 weeks	6700	6560

The capillary drainage time is a conventional test in which a 6.8 cm diameter circle is drawn on a 15 cm diameter sheet of Whatman size 41 filter paper, a plastic annulus (3.5 cm inside diameter, 4.2 cm outside diameter, 6.0 cm high) is placed vertically, concentric with the circle, on the filter paper, and the annulus is filled with the composition to be tested. Liquid from the composition is thereby absorbed into the filter paper and spreads slowly to the drawn circle. The time which elapses until the liquid contacts the circle is measured at three predetermined locations and an average value is calculated.

Examples 3a to 3d

Example 3a is a comparison example.

The following formulations given in Table 2 are prepared by mixing the ingredients in the order indicated. The compositions are then centrifuged at 275 G until there is no further increase in the volume of the clear separated liquid (continuous) phase and the resulting liquid is analyzed:

TABLE 2

Example	*3a*	*3b*	*3c*	*3d*
Ingredients				
deionized water	27.106			
colour	0.016			
sodium carbonate	6	4	2	0
potassium carbonate	0	2	4	6
STPP	21.106			
deionized water	14.184			
Attagel #50	4.00			
T_1O_2	0.444			
50% solution of NaOH	2.5			
47.5% solution of sodium silicate	13.684			
antifoam	0.16			
13% solution of NaOCl	10.0			
45% solution of surfactant	0.8			
	100.00			

Thus, the compositions are identical except for their K:Na ratios.

Properties of Product

Example	*3a*	*3b*	*3c*	*3d*
viscosity after 1 day at room temperature	8320	5520	4200	2120
after 3 weeks at room temperature	8550	6200	4500	2420
after ageing at 100° F (38° C) for 7 weeks	9400	8000	5600	3400
Specific gravity	1.37	1.37	1.40	1.39

Properties of liquid Obtained by Centrifuging

Example	*3a*	*3b*	*3c*	*3d*
viscosity at 25° C relative to water at 1 cps	4.4	4.4	4.8	6.3
% soluble silicate (calculated at mol ratio $Na_2O:SiO_2$ of 1:2.4)	7.5	7.3	7.3	7.1
% carbonate (calculated as Na_2CO_3)	8.8	8.5	7.4	6.6
% phosphate (calculated as $Na_5P_3O_{10}$)	1.7	2.5	3.7	6.1
specific gravity	1.257	1.262	1.276	1.30

The viscosities of the products for these Examples are measured with a Brookfield RVT viscometer spindle No. 5 at 80° F (26.7° C).

Examples 4-6 below illustrate a new and useful method for making the products described above (containing limited amounts of potassium). It can also be used for making other products of the type shown in U.S. application Ser. No. 497,615 (in which the potassium compound is not present) as well as other detergent slurries comprising fine particles of water-soluble inorganic builder salts dispersed in water containing dissolved builder salt, clay or other colloidal thickening agent, and surfactant. In these Examples (in which the particles of builder salt in the product are largely STPP hexahydrate plus hydrated sodium carbonate) there is formed a highly viscous (e.g. 20,000-60,000 cps viscosity) mixture of a limited amount of water, a highly alkaline saturated solution of builder salts and, as the major constituent, undissolved particles of water-soluble builder salt. This viscous mixture is subjected to grinding of the undissolved particles with a high speed disperser after which solid particles of the clay thickener are added and the clay is mechanically deagglomerated; thereafter the balance of the ingredients of the formula (e.g. other liquids or materials which readily dissolve or disperse in the liquid phase of high electrolyte content) may be mixed in. The mixture may then be subjected to additional high shear mechanical action to further deagglomerate the clay. It is found that with this method pre-dispersion of the clay in aqueous medium is not needed. The solid particles of clay readily disperse even though the medium is highly alkaline. The grinding of the undissolved builder salt particles takes place much more efficiently and rapidly in the substantial absence of the clay.

This subject matter is claimed in our copending application serial no........ filed .... with the present application.

In the method illustrated in Examples 4-6 the builder salt which is to constitute the major portion of the undissolved particles is preferably added to an aqeuous solution which already contains such a high concentration of dissolved other builder salt that this addition causes builder salt to be thrown out of solution (e.g. by common ion effect) and thus to recrystallize as tiny crystals.

Another significant feature of the mixing method illustrated in Examples 4-6 is the fact that it enables repeated batches of reproducible properties to be made using the entire "heel" of the previously formed batch as an ingredient of each successive batch.

As indicated earlier, the use of the process illustrated in Examples 4-6 is not limited to the making of compositions containing potassium salts. While it has thus far found its greatest utility in making formulations in which the clay is attapulgite, it may also be employed for compositions in which all, or part, of the clay is of the swelling type, e.g. a smectite type of clay such as bentonite (e.g. Gelwhite GP) or hectorite.

Example 4

In 32.0 parts of deionized water mixed with a small amount of a pigment (0.028 parts of Graphtol green, an aqueous paste containing 28% pigment) there are completely dissolved 2.0 parts K_2CO_3 (whose water solubility is over 100 parts per 100 parts of water even at 0° C and 5.0 parts granular sodium carbonate (whose water solubility is about 45 parts per 100 at 35° C). The solution has a temperature of about 90° F (32° C). Then 23.116 parts of powdered STPP containing about 0.5% water of hydration are added while continuously subjecting the mixture to the action of a high speed disperser. The amount of STPP is much more than that which is soluble in the amount of water present; its solubility in water is about 20 g per 100 ml at 25° C. In this Example, the STPP is a product of Olin Corp. having a phase I content of about 50%, a sodium sulphate content of about 2%, and a very fine particle size, it is a blend of powdered anhydrous STPP made by the known "wet process" and powdered STPP hexahydrate. On adding the STPP to the solution it hydrates rapidly, forming hard crystalline lumps comprising STPP hexahydrate. (It will be noted that 23 parts of STPP has the capacity, in forming the hexahydrate, to take up about 7 parts of water). The mixture is at first a thin slurry of undissolved STPP in a liquid which is a supersaturated solution. The temperature rises owing to the hydration reaction, reaching a peak of about 140° F (60° C). In about 3 to 4 minutes the mixture becomes much more viscous; its viscosity rises to above 20,000 cps (such as about 40,000-50,000 cps as measured at the slurry temperature e.g. with a Brookfield RVT, spindle #6 at 10 rpm). It is believed that during the process, sodium carbonate crystallizes (in the form of very fine crystals) out of the solution phase owing to the common ion effect (of the sodium of the STPP). When the mixture has become viscous the high speed disperser acts to grind the particles (e.g. of hydrated TPP) to a fine particle size, the grinding action is indicated, for one thing, by the increased power consumption of the disperser and an additional rise in temperature (e.g. to 150° F (66° C), which causes increased dissolution of builder salts; these will, in turn, recrystallize in fine form on cooling). This grinding is continued for about 5 minutes after the initial thickening of the slurry; during grinding the visible lumps of material disappear and the particle size of the undissolved particles is reduced so that, it is believed, substantially all the particles have diameters below 40 microns. Then a further 9.367 parts of water are added, lowering the viscosity to less than 10,000 cps (e.g. in the neighbourhood of 5000 cps, measured as indicated above), after which 3.3 parts of Attagel #50 and 0.732 parts of white TiO_2 (anatase) pigment are added to the highly alkaline mixture (whose pH is well over 9. e.g. 10.5) while the mixture is continuously subjected to the action of the high speed disperser, which disperses (deagglomerates) the clay to a large extent, so that the thick mixture becomes homogeneous and smooth in appearance. Then there are added 2.70 parts of 50% aqueous solution of NaOH, 0.16 parts of antifoam agent (Knapsack LPKN 158), 10.53 parts of 47.5% aqueous solution of sodium silicate (whose Na_2O:SiO_2 ratio is 1:2.4), 10.0 parts of a 12% aqueous solution of sodium hypochlorite and 0.8 parts of a 45% aqueous solution of a bleach-resistant anionic surfactant (Dowfax 3B2); these additions may be made under any desired mixing conditions, e.g. with simple stirring (although it may be convenient to continue the high shear dispersing action for such mixing). The mixture is then subjected to a milling action as by passing it through an in-line mill such as Tekmar "Dispax reactor" (which operates at a tip speed of 22 metres per second) which subjects the mixture to a high shear rate for a relatively short time (e.g. the "residence time" in the mill may be merely two seconds or less). The principal effect of this is to further deagglomerate the clay particles, as indicated by a significant increase in the yield value, e.g. raising the yield value of the mixture by some 33%.

The resulting mixture is thixotropic. It is believed that the particle size of the dispersed solid particles therein is so small that some 80% by weight, or more, have particle sizes below 10 microns. The mixture is at a temperature in the neighbourhood of 120-130° F (49-54° C) (at this temperature its viscosity is higher than at, say, 70° F (21° C)). It is drained off from the mixing vessel (e.g. from a bottom valve when the vessel has a conical bottom, or from a lower side valve of a substantially flat-bottomed mixing vessel). About 10% of the mixture remains as a "heel" in the vessel; owing to its flow characteristics it is difficult to remove all the composition from the vessel.

The entire procedure described above is then repeated over-and-over in the same mixing vessel without removing the heels at all.

The high-speed disperser may comprise a circular horizontal plate having alternately upwardly and downwardly extending circumferential teeth, which plate is mounted (on a vertical downwardly extending shaft) so as to rotate so rapidly that the circumferential speed (of the teeth) is more than about 75 feet per second (22.9 m/sec) (e.g. 90 feet per second (27.4 m/sec)). For laboratory operation a Cowles high speed disperser is suitable; for larger scale operation a Myers model 800 series high speed disperser may be used. These high speed dispersers reduce particles by impact grinding by the toothed plate and by laminar shear stress on the mixture. The shear generates heat in the batch, in addition to the heat generated by the dissolving, hydration, etc. At the resulting relatively high temperature the ingredients are more soluble and on crystallisation on cooling will give relatively small particles which do not settle rapidly if at all. The high speed disperser induces a "rolling" of the mixture i.e. the path of movement of the mixture is downward centrally of the vessel, outwardly along the rotating plate, upwardly along the side walls of the vessel and inwardly at the upper surface of the mixture. In the course of this movement desirable deaeration occurs, i.e. air (which is always introduced when powders are added) will leave the mixture during the inward leg of its circuit.

Apparently, after processing of the composition described above, crystal growth occurs to form many larger and relatively uniform-sized crystals (as shown by photomicrographs). Thus, Figure 4 indicates that crystals having diameters of the order of 80 microns are present. These crystals appear to contain polyphosphate but have not yet been fully identified.

Example 5

Example 4 is repeated except that the STPP powder is a Monsanto anhydrous STPP made by the known "dry process" and comprising anhydrous STPP humidified to the extent that its content of water of hydration is 1/2% (or somewhat higher, e.g. 1 1/2%). Its phase I content is about 20%. This STPP was also used in Example 3.

Example 6

Example 4 is repeated except that the initial proportion of water is 28.0 parts, the second proportion of water is 13.637 parts, and prior to the addition of the attapulgite clay there is added 1.11 parts of 45% aqeuous solution of sodium polyacrylate (Acrysol LMW-45N, having a molecular weight of about 4500). The amount of K_2CO_3 here is 3 parts and the amount of Na_2CO_3 is 4 parts.

The products of Example 4-6 were found to have the following characteristics:

	Example		
Properties	*4*	*5*	*6*
viscosity (cps)	4000	6000	4400
yield value (dynes/cm^2)	450	600	450
capillary drainage time (min)	8.2	5.6	6.1
centrifugal separation (%)	16	26.3	12
Thixotropy index	5	4.3	4.1

"Centrifugal separation" is measured by centrifuging at 275G as described in Example 3, above, and measuring the volume of the clear liquid layer in relation to the total volume.

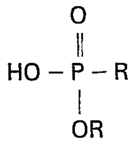
"Thixotropy index" is the ratio of the viscosity at 30 rpm to that at 3 rpm, measured at room temperature with a Brookfield HATD viscometer, #4 spindle.

In Example 6 a soluble chlorine bleach-resistant polymer is present. It is found that the presence of the polymer improves the resistance to separation of the product on standing or on centrifuging, without imparting a correspondingly large increase in the viscosity of the product. It will be appreciated that the polymer is present here in a very highly concentrated (saturated) electrolyte solution. It is also found that the presence of the polymer leads to improved protection of the overglaze layer of dishware (fine china). In work, thus far, these effects have been observed with polyacrylic acid salts, which have been found to be entirely compatible with chlorine bleach and with the clay in this system, e.g. the active chlorine content is maintained, as is the viscosity. Polymers of different molecular weights may be used; for instance, the polymer may have a molecular weight less than 10.000 or a molecular weight of 100,000 or more. Preferred molecular weights range from about 1,000 to 500,000. Molecular weights of from about 1000 to 50,000 are particularly notable for providing less filming on glass. The proportions of polymer may be in the range of 0.01 to 3% with the lower proportions being more suitable for the higher molecular weight polymers (e.g. 0.06% for a 300,000 molecular weight polymer). Other bleach-resistant polymers may be employed e.g. Tancol 731 which is a sodium salt of a polymeric carboxylic acid having a M.W. of about 15000.

This subject matter is claimed in our copending application serial no....... filed .... with the present application.

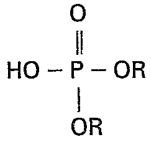
The STPP preferably employed in the composition in a range of about 8 to 35 wt %, preferably about 20 to 30 wt %, should preferably be free of heavy metal which tends to decompose or inactivate the preferred sodium hypochlorite and other chlorine bleach compounds. The STPP may have an average degree of hydration of less than about 1 or more than about 5 e.g. 0.to 2.7% by weight or at least 16.5% of water, including the stable hexahydrate with a degree of hydration of 6 corresponding to about 18% by weight of water or more. Actually, humidification to an average of about 0.3 to 1% water is highly effective, serving it is thought to form seeds of the stable hexahydrate which expedites hydration and solubilization of the remaining STPP particles.

Foam inhibition is important to increase dishwasher machine efficiency and minimize destablizing effects which might occur due to the presence of excess foam within the washer during use. Foam may be sufficiently reduced by suitable selection of the type and/or amount of detergent active material, the main foam-producing component. The degree of foam is also somewhat dependent on the hardness of the wash water in the machine whereby suitable adjustment of the proportions of STPP which has a water-softening effect may aid in providing the desired degree of foam inhibition. However, it is generally preferred to include a chlorine bleach stable foam depressant or inhibitor. Particularly effective are the alkyl phosphonic acid esters of the formula



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

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



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

available for example from Hooker (SAP) and Knapsack (LPKn-158), in which one or both R groups in each type of ester may represent independently a $C_{12\text{-}20}$ alkyl group. Mixtures of the two types, or any other chlorine bleach stable types, or mixture of mono- and di-esters of the same type, may be employed. Especially preferred is a mixture of mono- and di-$C_{16\text{-}18}$ alkyl acid phosphate esters such as monostearyl/distearyl acid phosphates 1.2/1 (Knapsack). When employed, proportions of 0.1 to 5 wt %, preferably about 0.1 to 0.5 wt %, of foam depressant in the composition is typical, the weight ratio of detergent active component (d) to foam depressant (e) generally ranging from about 10:1 to 1:1 and preferably about 4:1 to 1:1. Other defoamers which may be used include for example the known silicones.

Although any chlorine bleach compound may be employed in the compositions of this invention, such as dichloro-isocyanurate, dichloro-dimethyl hydantoin, or chlorinated TSP, alkali metal, e.g. potassium, lithium, magnesium and especially sodium, hypochlorite is preferred. The composition should desirably contain sufficient chlorine bleach compound to provide about 0.2 to 4.0% by weight of available chlorine, as determined for example by acidification of 100 parts of the composition with excess hydrochloric acid. A solution containing about 0.2 to 4.0% by weight of sodium hypochlorite contains or provides roughly the same percentage of available chlorine. About 0.8 to 1.6% by weight of available chlorine is especially preferred.

The sodium silicate, which provides alkalinity and protection of hard surfaces such as fine china glaze and pattern, is preferably employed in an amount ranging from about 2.5 to 20 wt %, preferably about 5 to 15 wt %, in the composition. The sodium silicate is generally added in the form of an aqueous solution, preferably having an Na_2O:SiO_2 ratio of about 1:2.2 to 1:2.8. At this point it should be mentioned that most of the other components of this composition, especially NaOH, sodium hypochlorite, foam depressant and thixotropic thickener, are also often added in the form of a preliminarily prepared aqeuous dispersion or solution.

Detergent active material useful herein must be stable in the presence of chlorine bleach, especially hypochlorite bleach, and preferably comprise those of the organic anionic, amine oxide, phosphine oxide, sulphoxide or betaine water-dispersable surfactant types, the first mentioned anionics being most preferred. They are preferably used in amounts ranging from about 0.1 to 5% preferably about 0.5 to 2.0%, more preferably about 0.3 to 0.8%. Particularly preferred surfactants herein are the linear or branched alkali metal mono- and/or di-($C_{8\text{-}14}$) alkyl diphenyl oxide mono- and/or disulphonates, commercially available for example as DOWFAX (Registered Trade Mark) 3B-2 and DOWFAX 2A-1. In general, the paraffin sulphonates tend to impair, if not destroy thixotropy, having been found to unduly increase viscosity causing severe shearing force problems. In addition, the surfactant should be compatible with the other ingredients of the composition. Other suitable surfactants include the primary alkylsulphates, alkylsulphonates, alkylarylsulphonates and sec.-alkylsulphates. Examples are sodium 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 dodecyl-benzenesulphonate. The corresponding potassium salts may also be employed.

As other suitable surfactants or detergents, the amine oxide surfactants are typically of the structure R_2R^1NO, in which each R represent a lower alkyl group, for instance methyl, and R^1 represents a long chain alkyl group having from 8 to 22 carbon atoms, for instance a lauryl, myristyl, palmityl or cetyl group. Instead of an amine oxide, a corresponding surfactant phosphine oxide R_2R^1PO or sulphoxide RR^1SO can be employed. Betaine surfactants are typically of the structure $R_2R^1N^+R''COO^-$, in which each R represents a lower alkylene group having from 1 to 5 carbon atoms. Specific examples of these surfactants are lauryldimethylamine 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.

Thixotropic thickeners, i.e. thickeners or suspending agents which provide an aqueous medium with thixotropic properties, are known in the art and may be organic or inorganic water soluble, water-dispersible or colloid-forming, and monomeric or polymeric, and should of course be stable in these compositions, e.g. stable to high alkalinity and chlorine bleach compounds such as sodium hypochlorite. Those specially preferred generally comprise the inoganic, colloid-forming clays of smectite and/or attapulgite types. These materials are generally used in amounts of about 1.5 to 10, preferably 2 to 5 wt % but in any event in an amount sufficient to confer the desired thixotropic properties.

Smectite clays include montmorillonite (bentonite), hectorite, saponite, and the like. Materials of this type are available under trade names such as Thixogel (Registered Trade Mark) No. 1 and Gelwhite (Registered Trade Mark) GP from Georgia Kaolin Company (both being montmorillonites). Attapulgite clays include the materials commercially availabe under the trade name Attagel (Registered Trade Mark), i.e Attagel 40, Attagel 50 and Attagel 150 from Engelhard Minerals and Chemicals Corporation. Mixtures of smectite and attapulgite types in weight ratios of 4:1 to 1:5 are also useful herein. Thickening or suspending agents of the foregoing types are well known in the art, being described, for example, in U.S. Patent No. 3,985,668 referred to above. Abrasives or polishing agents should be avoided.

The amount of water contained in these compositions should of course be neither so high as to produce unduly low viscosity and fluidity, nor so low as to produce unduly high viscosity and low flowability, thixotropic properties in either case being diminished or destroyed. Such amount is readily determined by routine experimentation in any particular instance, generally ranging from about 45 to 75 wt %, preferably about 55 to 65 wt %. The water should also be preferably deionized or softened.

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

Other conventional ingredients may be included in these compositions in small amounts generally less than about 3 wt % such as perfume, hydrotropic agents such as the sodium benzene, toluene, xylene and cumene sulphonates, preservatives, dyestuffs and pigments and the like, all of course being stable to chlorine bleach compounds and high alkalinity (properties of all the components). Especially preferred for colouring are the chlorinated phthalocyanines and polysulphides of aluminosilicate which provide, respectively, pleasing green and blue tints. TiO_2 may be employed for whitening or neutralizing off-shades.

The liquid ADD compositions of this invention are readily employed in known manner for washing dishes, other kitchen utensils and the like in an automatic dish washer, provided with a suitable detergent dispenser, in an aqueous wash bath containing an effective amount of the composition.

It is understood that the foregoing detailed description is given merely by way of illustration and that variations may be made therein without departing from the spirit of the invention.

CLAIMS

1. An aqeuous thixotropic automatic dishwasher composition comprising a liquid phase which is water containing dissolved alkali metal tripolyphosphate, alkai metal silicate and dispersed non-swelling clay thickener and a solid phase which is mainly sodium tripolyphosphate, the composition containing potassium ions in an amount such that the K:Na weight ratio is in the range of about 0.04 to 0.5.
2. A composition as claimed in Claim 1 having a yield value of at least 200 dynes/cm^2.
3. A composition as claimed in Claim 1 or Claim 2 containing a chlorine bleach, an alkali metal carbonate and a bleach-resistant surfactant.
4. A composition as claimed in Claim 1, 2 or 3 in which the said composition contains about 20 to 25% sodium tripolyphosphate.
5. A composition as claimed in Claim 3 or Claim 4 in which the alkali metal carbonate is potassium carbonate.
6. A composition as claimed in any one of Claims 1 to 5 in which potassium tripolyphosphate is present.
7. A composition as claimed in any one of Claims 1 to 6 including potassium pyrophosphate.
8. A composition as claimed in Claim 1 substantially as specifically described herein with reference to the examples.

9. An aqueous thixotropic automatic dishwasher composition as claimed in any one of the preceding claims comprising approximately by weight:

(a) as ingredient A, 5 to 35% alkali metal tripolyphosphate;

(b) as ingredient B, 2.5 to 20% sodium silicate;

(c) optionally, as ingredient C, 0 to 9% alkali metal carbonate;

(d) as ingredient D, 0.1 to 5% chlorine bleach stable, water-dispersible organic detergent active material;

(e) optionally, as ingredient E, 0 to 5% chlorine bleach stable foam depressant;

(f) as ingredient F, chlorine bleach compound in an amount to provide about 0.2 to 4% of available chlorine;

(g) as ingredient G, thixotropic thickener in an amount sufficient to provide the composition with a thixotropy index of about 2.5 to 10; and

(h) optionally, as ingredient H, 0 to 3% of sodium hydroxide, the composition containing potassium ions in an amount such that the K:Na weight ratio is in the range of about 0.04 to 0.5.

10. An aqueous thixotropic automatic dishwasher composition comprising, approximately by weight:

(a) as ingredient A, 8 to 35% alkali metal tripolyphosphate which prior to addition to the composition had a degree of hydration of less than 1;

(b) as ingredient B, 2.5 to 20% sodium silicate;

(c) as ingredient C, 2 to 9% sodium carbonate;

(d) as ingredient D, 0.1 to 5% chlorine bleach stable, water-dispersible organic detergent active material;

(e) optionally, as ingredient E, 0 to 5% chlorine bleach stable foam depressant;

(f) as ingredient F, sodium hypochlorite in an amount to provide about 0.2 to 2% of available chlorine;

(g) as ingredient G, 1.5 to 10% thixotropic smectite and/or attapulgite clay thickener sufficient to provide the composition with a thixotropy index of about 2.5 to 10; and

(h) as ingredient H, sodium hydroxide in an amount sufficient to provide the composition with a pH of about 10.5 to 13.5, the composition containing potassium ions in an amount such that the K:Na weight ratio is in the range of about 0.04 to 0.5.

11. A method comprising washing dishes in an automatic dishwasher with an aqueous wash bath containing an effective amount of a composition as claimed in any one of Claims 1 to 10.

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