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㊴ **High-carbonate automatic dishwashing detergent with decreased calcium salt deposition.**

㊷ An automatic dishwashing detergent primarily comprised of an alkali-metal carbonate as the sole builder, alkali-metal silicates, and a calcium precipitation inhibitor system consisting of a low foaming surfactant, a low molecular weight polycarboxylic acid, and a small amount of a threshold inhibition agent. Optionally halogen, peroxygen or peracid bleaching species enzymes, fragrances, dyes and other adjuncts may be included. The composition provides good cleaning performance especially on starchy soils, and no appreciable calcium precipitates results, even in water having a hardness of at least about 400 ppm.

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HIGH-CARBONATE AUTOMATIC DISHWASHING DETERGENT WITH DECREASED CALCIUM SALT DEPOSITION

The invention relates to machine ware washing compositions, and particularly to such compositions having high levels of alkali-metal carbonate as essentially the only builder.

Automatic dishwashing detergents (ADWDs) typically include a variety of specialized components for specific purposes during the multi-step wash cycle. Surfactants may be present for detergency and/or as rinse aids. Silicates act to provide alkalinity and to prevent corrosion. Bleaches are often included for oxidizing power. Abrasives may be included to provide scouring action. Builders are important to improve washing performance, and must be selected to avoid precipitation of calcium salts on wares. Typically, silicates, carbonates, phosphates or mixtures thereof are employed as builders. For ware washing applications, the builder materials may provide alkalinity and buffering capacity, prevent flocculation, maintain ionic strength, extract metals from soils and remove alkaline-earth metal ions from washing solutions. Phosphates are extremely effective in these applications, however, there is a relatively high cost associated with their use. Additionally, phosphates are disfavored owing to their eutrophication effect on lakes and streams, and may be regulated in some states. Silicates are not preferred becausethey are costly, and at the generally high levels required, are potentially toxic. High levels of alkali-metal carbonates have been found to be very effective in ware washing applications, and have proven to be superior in performance to phosphates in the removal of starchy soils, one of the principal soils found on tablewares. A drawback associated with such high carbonate levels, however, is that calcium ions present in the washing water readily form precipitates with the carbonates. Various approaches have been employed to combat the formation of calcium precipitates. Complexing agents such as zeolites can be added and can be effective at removing calcium. These have limited use in ware washing compositions, however, as these zeolites are substantially insoluble, and may themselves deposit on tablewares. Polymeric sequestering agents such as polyacrylates and polyether carboxylates can also be employed, but since these also act to complex the calcium, generally high levels are required. Sequestering and complexing agents tend to be expensive, adding significantly to the overall cost. Schroeder, DE 3001937, discloses a granular ADWD with 50-70% sodium carbonate, a poly (alpha-hydroxy acrylic acid), phosphonate threshold inhibitors and alkyl phosphate esters. Becker et al, GB 1536136, describes a laundry detergent including a phosphonic or polyacrylic acid sequestrant, a protective colloid and a maximum of 30% phosphate builder, with an optional carbonate builder.

Unsubstituted polyacrylic acids used with 20-60% sodium carbonate are described in US 3579455 issued to Sabatelli and US 3627686 issued to Brungs. Brungs and Sabatelli use relatively high levels of NTA and hexametaphosphate, respectively, to complex calcium. US 4539144, to de Ridder et al describes ADWDs with no or low phosphates and with 5-50% of a sequestrant, 0.05-5% of poly (maleic acid) and may have a sodium carbonate builder. Low molecular weight polyacrylates without other chelating agents are used to inhibit calcium carbonate deposition by ADWDs in Chakrabarti, US 4203858.

In EP 266904 (Frankena) sodium carbonate is combined with polyacrylate, phosphonates, and a dipicolinic acid complexing agent. Similarly, in US 3850852 issued to Neillie et al sodium carbonate can be combined with polyacrylates, phosphonates, and a calcium sequestering agent.

US 4687592 to Collins et al describes carbonate, polyacrylate, phosphonates, and a calcium sequestering agent which is an ether polycarboxylate and comprises a major part of the formula. The polyacrylate is added to disperse soils and the phosphonate is added to chelate iron and manganese. phosphonates and polyacrylates are also mentioned as possible co-builders in GB 2194546 to Laitem et al and US 4588515 to Schuh et al. In both patents, STPP is the preferred builder.

Generally, high carbonate detergents are not preferred in the art. When high carbonate levels are used, relatively high levels of complexing agents are used to prevent the formation of calcium carbonate precipitates. Often the complexing agents themselves offset any advantages gained by use of carbonates as builders.

In view on the art, there remains a need for an alkali-metal carbonate based ware washing composition which prevents the deposition of calcium salts by inhibiting the formation of calcium precipitates, rather than by sequestering or complexing.

It is therefore an object of the present invention to provide a high carbonate ware washing composition having acceptably low levels of calcium precipitates.

It is another object of the present invention to provide a ware washing composition which is superior in performance in removing starchy soils.

It is another object of the present invention to provide a highly effective dishwashing detergent which avoids the use of potentially toxic materials.

It is another object of the present invention to provide a ware washing composition which does not utilize high levels of Phosphate builders.

It is yet another object of the present invention to provide a highly cost-effective detergent composition.

SUMMARY OF THE PRESENT INVENTION

In one embodiment, the invention comprises a dry granular automatic dishwashing detergent consisting of:

(a) an alkali-metal carbonate;
(b) a alkali-metal silicate;
(c) an inhibitor system; and
(e) a low-foaming surfactant

Optionally, a halogen or peroxygen bleaching species can be included for oxidizing power.

The automatic dishwash detergent of the present invention is primarily comprised of sodium or potassium carbonates and silicates, low levels of an inhibition system comprising a low molecular weight polycarboxylic acid and a threshold inhibition agent, and a low foaming surfactant. Polymers and copolymers of acrylic and methacrylic acids with weight average molecular weights between 1,000 and 10,000 are the preferred polycarboxylic acids. Suitable threshold inhibition agents (TIAs) include monomeric phosphonate-containing organic compounds, inorganic oligomeric phosphates, and mixtures thereof. Preferred TIAs include polyphosphonates such as the Monsanto Company's trademarked DEQUEST series, phosphonated polycarboxylic acids such as Mobay Chemicals trademarked BAYHIBIT series, and phosphonocarboxylic acids. No other calcium complexing agents or builders such as sodium tripolyphosphate present in the detergent.

It is therefore an advantage of the present invention that high levels of phosphates are avoided.

It is another advantage of the composition of the present invention that the carbonate builder provides superior starchy soil removal without appreciable precipitation of calcium salts.

It is a further advantage of the present invention that the composition is more cost-effective than other builder systems.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Alkali-Metal Carbonate

The alkali-metal carbonate is the primary and preferably the only builder material of the composition of the present invention. Alkali-metal carbonates, sesquicarbonates and bicarbonates are suitable, and preferred are sodium and/or potassium carbonates. At least about 30%, preferably 40%, most preferably 60% carbonate is needed. As used herein unless otherwise stated all percentages are weight percentages. Higher levels of carbonates will function, however, at levels greater than about 80% there is insufficient room for the other ingredients which contribute to the overall effectiveness of the composition. The carbonate acts as a builder to remove calcium and additionally provides alkalinity and aids in soil removal. At the high levels disclosed herein, the alkali-metal carbonate provides superior starchy soil removal compared to other builders such as phosphates.

Alkali-Metal Silicate

One component of the present invention is an alkali-metal silicate, specifically one having the formula: $M_2O(SiO_2)_n$ where M represents an alkali-metal, and n is between about 1 and 4. Preferred alkali-metal silicates are sodium, potassium and lithium silicates, with sodium silicate being the most preferred, and with a preferred n value of 2.0-2.4. A most preferred maximum value for n is about 3.2 in order to minimize insoluble silicates during storage. It is further preferred that at least about 10% of the total silicates have an n value of greater than about 1.6 to impart suitable anti-corrosive properties. Examples of other suitable silicates include sodium or potassium orthosilicates and metasilicates. As used hereinafter, the term "silicate" will be taken to mean any of these alkali-metal silicates, individually or combined.

Mixtures of any of the foregoing alkali-metal silicates are also suitable. The alkali-metal silicate is present in an amount of from about 2% to 30%, preferably about 5% to 10%. A minimum of about 2% silicate is necessary to provide adequate corrosion resistance. Preferred commercially available sodium silicates are sold by the Philadelphia Quartz Corporation under the Trademarks RU, as a 47% solution, and D, as a 44.1% solution. In addition to their anti-corrosive effects, the silicates provide alkalinity and serve as granulating aids to increase particle size of the agglomerates. Sodium silicates are known to be very effective at cleaning, especially when used on oil and grease stains.

Inhibitor System

The inhibitor system, comprising a polycarboxylic acid, or salt, in conjunction with low levels of a threshold inhibition agent, acts to inhibit significant calcium precipitates, resulting in aesthetically pleasing tablewares. A preferred polycarboxylic acid is a polyacrylic or polymethacrylic acid homopolymer. Copolymers such as acrylic/maleic and acrylic/hydroxyacrylic acids also function well. A preferred weight average molecular weight range is about 1000-10,000 g/mole, more preferred is about 2000-5000 g/mole. The weight average molecular weight range for acrylic/maleic acid copolymers is about 5000-50,000 g/mole, depending on the amount of maleic acid present.

It is preferred to add the polycarboxylic acid in fully neutralized form, e.g. as a sodium or potassium salt, however, the acid form is equally effective in preventing the deposition of calcium salts. It is noted that for the purpose of the present invention the acid forms are equivalent to the salt forms except where the acid has limited solubility. It is also noted that except where explicitly stated or implied from the context, the acid and salt forms are used interchangeably. It is further noted that if added as salt, the required weight percentage range will be higher than that of the acid, owing to the presence of the counterion. For example about a 30% greater weight percentage of sodium polyacrylate is needed compared to the acid form. An example of a commercial source of the polycarboxylic acids is the Rohm and Haas Company's ACRYSOL polyacrylates. Preferred are ACRYSOL LMW-20N and LMW-45N, fully neutralized polyacrylic acids, sodium salts, having weight average molecular weights of about 2,000 and 4,500 g/mole, respectively. About 0.1-10% polycarboxylic acid is present, preferably about 3-8%. Higher levels of polycarboxylic can be added, but they do not appear to correspondingly improve inhibition of calcium precipitates.

The other component of the inhibitor system is the threshold inhibition agent, (TIA), which at low levels, i.e. about 0.1-5 percent, synergistically acts with the polycarboxylate to prevent the formation of calcium precipitates on wares washed with the composition. Suitable threshold inhibition agents include monomeric phosphonate containing organic compounds, inorganic oligomeric phosphates, and mixtures thereof. Specific examples of the foregoing include poly phosphonates/carboxylates of mono-, di-, and tri- alkylamines having at least one phosphonate group; 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP); aminotri-(methylenephosphonic acid) (ATMP); sodium hexametaphosphate (SHMP); 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC); phosphonohydroxy acetic acid, similar compounds, and mixtures thereof. TIAs are most preferably HEDP, ATMP, SHMP, PBTC, similar compounds, and mixtures thereof. A preferred level for TIA is about 0.1-3.5%, and more preferred is 0.3-2.0%. The TIA generally should be kept at low levels for to minimize the amount of phosphorous in the system and to minimize cost. Two percent TIA corresponds to a level in the wash (assuming 10 L of wash water) of about 60 ppm. Generally, increasing TIA levels in the main wash above about 60 ppm does not yield a corresponding increase in effectiveness, thus the lower levels are more cost-effective. Finally, if too much phosphonate is present, it can form a precipitate with calcium. The TIA/polymer system is effective at preventing observable calcium precipitates on wares in waters having hardness levels at least to about 400 ppm. The TIA may be added as an acid, or as salt, such as sodium or potassium. The inhibitor system is added at a level necessary to inhibit the precipitation of calcium salts on the wares. The exact level will vary with water hardness and type of polycarboxylic acid and TIA. It is noted that generally, increasing the level of polycarboxylic acid allows for a decrease in the level of TIA, and vice versa. It is again noted that the acid and salt forms are equivalent except where the acid has limited solubility. It is also again noted that the foregoing TIA weight percentage ranges are based on the acid forms; more may be required if salts are used.

Low Foaming Surfactant

A low-foaming surfactant is included to provide detergency during the wash phase of the machine wash cycle, and to promote "sheeting" during rinse, i.e. uniform runoff of the rinse water. The surfactant further acts to emulsify oily soils and suspends solids to prevent their redeposition. Since machine dishwashers utilize the mechanical effects of water sprays to remove a significant amount of solids, the surfactant must not produce foams, which impair this mechanical cleaning action. Preferably the surfactant will reduce or inhibit foams which are produced by food soils.

Preferred surfactants are nonionics, especially C_{1-4} alkoxylated aliphatic alcohols and C_{1-4} alkoxylated alkyl phenols. Particularly preferred are ethoxylated/propoxylated C_{8-14} alcohols. There should be at least about ten alkoxy groups per alcohol, preferably at least about twenty. Examples of preferred ethoxylated/propoxylated aliphatic alcohols are BASF Corporation's trademarked INDUSTROL, and PLURAFAC. Certain C_{1-4} alkylene oxide copolymers such as ethylene oxide/propylene oxide copolymers are also preferred as surfactants. These are exemplified by BASF's trademarked PLURONIC series. Optionally, the terminal hydroxyls of any of the foregoing can be replaced by an ether, e.g. a C_{1-4} alkyl or a benzyl ether, or by a halogen, to further reduce foaming. Other suitable surfactants are disclosed in US 4306987 and 4272394 both issued to Kaneko and assigned to BASF Wayandotte Corporation, the disclosures of which are incorporated herein by reference.

It is also within the scope of the invention herein to utilize a mixture of surfactants all of which may not be low-foaming as long as the mixture is low-foaming by, e.g. including a foam suppressant such as monostearyl phosphate or other materials as known in the art. As used hereinafter, "low-foaming surfactant" will be taken to mean an individual low-foaming surfactant, or a mixture of two or more surfactants, or surfactants and foam suppressants, yielding low foaming. The surfactant is added at a level of about 0-10 percent, preferably about 1-5 percent.

Optional Ingredients

Various adjuncts can be added, as known in the art. Examples include fragrances, dyes or pigments, enzymes such as proteases, lipases and amylases, additional corrosion inhibitors, etc. Water may be present up to about 15%, and can be present as free water or as water of hydration of the inorganic salts such as sodium carbonate. Some water may be deliberately added as a filler. Additionally, filler materials include inorganic salts such as sodium or potassium sulfates, nitrates, borates and chlorides, and organic materials like sugars.

It may be desirable to adjust the pH of the wash water by including an electrolyte/buffer Generally, these are alkali-metal inorganic acid salts, hydroxides or oxides. It may also be suitable to use such materials as aluminates and organic materials, such as gluconates, citrates, succinates, maleates, and their alkali metal salts. The electrolyte/buffer should maintain the wash pH range within a range of between about 8.0 to 13.0, more preferably about 9.0 to 12.0. Sodium hydroxide is preferred as it does not interact adversely with any other ingredients, and is very cost effective. It is noted that the silicates and carbonates can also act to keep the wash pH range within the desired limits. The amount of electrolyte/buffer added solely for purposes of buffering can vary from about 0% to 10%.

A particularly preferred adjunct is a bleach, which may be selected from various halogen, peroxide or peracid bleaches. The bleach can remove organic stains, aids in soil removal and helps to prevent spotting and filming. Most bleaches, in fact, perform well in the relatively high temperatures associated with automatic dishwashers. Examples of halogen bleaches include the alkali metal and alkaline earth salts of hypohalite, haloamines, haloimines, haloimides and haloamides. All of these are believed 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, chlorinated trisodium phosphate, potassium and sodium dicholoroisocyanurate, trichlorocyanuric acid, and their hydrates. Also suitable are hydantoins, such as dibromo and dichloro dimethyl-hydantoin, chlorobromodimethyl hydantoin, N-chlorosulfamide (haloamide), chloramine (haloamine), N-brominated and N-chlorinated succinimide, malonimide, pthalimide and napthalimide. Peroxygen bleaches also are effective. Sodium perborate is a particularly useful bleach source, and may be formulated as a mono- or tetra- hydrate. Preferred peroxygen bleaches are available in solid form and include sodium percarbonate, sodium perborate, sodium phosphate peroxyhydrate, potassium permonosulfates and metal peroxides. Bleach activators, also known as peracid precursors can be included with the peroxygen compounds. Examples of activators include tetraacetyl ethylenediamine (TAED), and nonanoyloxy benzenesulfonate (NOBS). Peracid bleaches (including monoperacids and diperacids) may be advantageous in terms of bleaching performance. Suitable peracid bleaching species include C_{8-12} alkyl peracids, especially perazelaic and diperazelaic acids, diperoxydodecanedioic acid (DPDDA), and alkyl monoperoxysuccinic acid. Peracid bleaching species, and a method for their production, are described in U. S. patent 4,337,213 issued June 29, 1982 to Marynowski et al, the disclosure of which is incorporated herein by reference. DPDDA is particularly preferred for use in the composition of the present invention as it is relatively storage stable and produces desirable bleaching results. If added, the bleach is present in an amount sufficient to provide effective bleaching, e.g., from about 0 to 10% by weight active, more preferably from about 0.05 to 5% by weight active and most preferably from about 1 to 3% by weight active depending on the bleaching species chosen.

The dishwashing detergent composition is prepared by any means known in the art to yield a dry, free-flowing granular mixture, such as agglomeration or spray drying. Agglomeration is preferred. An O'Brien rotary drum agglomerator was used in the following agglomeration example. Sodium carbonate and sodium sulfate filler (if desired) is initially charged to the agglomerator. Three liquid additions are made during each batch. Spray rates and atomizing air pressures can be set for each liquid addition to suit desired finished product properties. The first liquid to be sprayed is the low-foaming surfactant, sprayed at a rate of 0.5 pounds/min. The second liquid addition is a preblend consisting of the TIA, polymer, and sodium hydroxide, and is applied at a preferred rate of 1.0 pound/min. The final liquid addition is sodium silicate, which can be applied at ambient or elevated temperature, and at a rate of 1.0 pound/min. The product may be dried/conditioned at the completion of the agglomeration. Static drying, fluid bed drying, and rotary drum conditioning may all be applied. Static drying typically consists of holding the agglomerated product at 140° F for 24 hours, while fluid bed drying may be performed for 30 minutes at 140° F. Finished product densities range between 0.6g/cm^3 to 1.0 g/cm^3. An example formula is shown below.

Example I

Ingredient	Wt.% Active
Alkali metal carbonate	30-80
Low-foaming surfactant	0-10
Bleaching agent	0-10
Alkali metal silicate (SiO_2/M_2O = 2-3)	5-30
Filler (sulfate, chloride, nitrate salts)	0-50
Polycarboxylic acid	0.1-10
TIA	0.1-5
Water	0-15

EXPERIMENTAL RESULTS

The various soils of TABLES I-IV were tested, generally, by the procedure of cooking the soil, applying it to dishes or glasses, and allowing it to cool and dry. Thus, the oatmeal and starch soils were prepared in accordance with their package directions and/or intended use, spread onto plates, and allowed to dry. Milk and pudding soils were cooked into beakers, and allowed to dry. Soil removal was visually graded, against photographic standards, on a scale of 1 to 10, with 10 being complete removal of soil. All soil removal evaluations herein were performed after one wash cycle.

Machine dishwashing filming and spotting evaluated in Tables I-IV was measured by ASTM Tentative Method D3556-76T (CSMA DCC-05), the disclosure of which is fully incorporated by reference herein. To summarize, clean glass tumblers are loaded into an automatic dishwasher, along with 4 plates, each soiled with 10g of a standard soil comprising powdered nonfat milk, margarine, and a cereal solution. Thirty grams of detergent was added to the closed cup for release in the main wash. Typically, the main wash utilizes 7-12 liters of water, which dissolves the detergent. The wares were washed in the dishwasher for 5 cycles, with the soils and detergent renewed after each cycle. The tumblers were rated visually in a light box, on a 5 point scale, for filming and spotting. The results were scored as follows:

Rating	Spotting	Filming
1	glass spotless	no film
2	spots at random	barely perceptible
3	1/4 of glass covered with spots	slight film
4	1/2 of glass covered with spots	moderate film
5	glass completely covered with spots	heavy film

TABLE I compares soil removal of three builders: sodium carbonate of the present invention, sodium citrate and an acrylic/maleic copolymer. The effect of high carbonate levels on various soils is advantageously shown herein. All formulas have 7.5% sodium silicate (SiO_2/Na_2O = 2.4), 4% low-foaming surfactant (an ethoxylated/propoxylated C_9 aliphatic alcohol), 1% sodium dichloroiscocyanurate, and water. Wash conditions included 30 grams of detergent added to the main wash, 120° F wash water having a 125 ppm water hardness (as $CaCO_3$; Ca/Mg = 3).

TABLE I

SOIL REMOVAL OF NO-PHOSPHATE BUILDERS					
	Wt.%				
Example	Na_2CO_3	Sodium Citrate	Acrylic/maleic Copolymer (1)		
1	75.0	0.0	0.0		
2	0.0	75.0	0.0		
3	0.0	0.0	75.0		
4	37.5	37.5	0.0		
5	37.5	0.0	37.5		
6	0.0	37.5	37.5		
	Visual Grade				
Example	Starch	Oatmeal	Milk	Pudding	Average
1	4.0	8.3	5.8	4.8	5.7
2	0.9	5.4	3.5	3.3	3.3
3	1.0	5.7	3.3	2.3	3.1
4	4.6	7.3	4.2	3.7	5.0
5	1.6	7.5	3.9	4.9	4.5
6	0.5	5.1	3.7	3.3	3.2
LSD_{95}	1.7	1.2	1.5	2.0	0.8

(1) SOKALAN CP-5P, a trademarked product of by BASF Corporation, which is a sodium salt of an acrylate/maleate copolymer, with a weight average molecular weight about 70,000.

Tables IIA-B illustrate the beneficial absence of spotting/filming on wares washed with the composition herein. The effects of polycarboxylate and TIA on inhibition of calcium precipitation was measured by evaluating spotting and filming on glassware washed with two compositions of the present invention. The compositions included Na_2CO_3 (68% in the composition of IIA and 60% in that of II-B), 8% sodium silicate (SiO_2/Na_2O = 2.4), 4% low-foaming surfactant, 2% sodium dichloroiscocyanurate, with the remainder water. The Table II-B composition also included about 1.4-11.9% Na_2SO_4 filler, and 0.5% NaOH. Wash conditions were 30 grams of detergent added to the main wash, and 140° F wash water, with the hardness as indicated in each Table. The glasses were graded after 5 cycles using the ASTM D3556-76T method.

TABLE II-A

EFFECT OF INHIBITOR SYSTEM ON SPOTTING AND FILMING IN 100 PPM HARDNESS WATER				
	Weight Percent Active		Visual Grades	
Example	Sodium Polyacrylate(1)	Na_5PBTC(2)	Spots	Film
1	1.87	0.21	2.2	4.1
2	10.57	0.21	2.3	2.6
3	1.87	1.21	2.4	2.4
4	10.57	1.21	2.1	2.7
5	0.00	0.71	2.1	3.1
6	12.44	0.71	2.2	2.8
7	6.22	0.00	2.0	4.6
8	6.22	1.43	2.9	2.4
9	6.22	0.71	2.3	3.4
Control(3)			1.9	2.6
LDS_{95}			0.8	1.1

(1) Weight average molecular weight of about 2000 g/mole.
(2) Na_5PBTC = Pentasodium 2-phosphonobutane-1,2,4-tricarboxylate.
(3) As CASCADE detergent, a trademarked product of the Procter & Gamble Co., having 8.3% phosphorus.

TABLE II-B

EFFECT OF INHIBITOR SYSTEM ON SPOTTING AND FILMING IN 300 PPM HARDNESS WATER				
	Weight Percent Active		Visual Grades	
Example	Sodium Polyacrylate(1)	Na_5PBTC(2)	Spots	Film
10	1.50	0.86	2.5	3.8
11	9.00	0.86	2.8	3.4
12	1.50	1.64	2.4	3.1
13	9.00	1.64	2.0	2.9
14	0.00	1.25	3.1	4.1
15	10.50	1.25	1.7	3.5
16	5.25	0.71	1.9	3.4
17	5.25	1.78	2.0	3.1
18	5.25	1.25	2.1	3.1
Control(3)			1.5	2.2
LDS_{95}			0.3	0.9

(1) Weight average molecular weight of about 2000 g/mole.
(2) Na_5PBTC = Pentasodium 2-phosphonobutane-1,2,4-tricarboxylate.
(3) As CASCADE detergent, a trademarked product of the Procter & Gamble Co., having 8.3% phosphorus.

A comparison of examples 1-4 shows that both polymer and TIA are effective in reducing filming. Some TIA is, however, necessary to inhibit film formation, as shown by example 7, with no TIA. Example 5 with no polymer, in 100 ppm hardness water, resulted in a spotting grade of 2.1, not significantly different from the control at the 95% confidence level. With harder water, however, the absence of polymer results in pronounced spotting, as seen in example 14. The polymer thus is of greater importance in harder water.

Table III shows the performance benefit that the high carbonate levels have on soil removal, with particular emphasis on starch and pudding soil removal, compared to a phosphorus-containing formula of the art. Also shown is the added soil removal benefit imparted by the polyacrylate of Formula C on starchy soil removal.

Table IV demonstrates the great difference in spotting/filming made by the inclusion of the inhibitor system of the present invention. Formula B, with no inhibitor system, resulted in spotting and filming grades of more than five, a wholly unacceptable result from a commercial viewpoint. Formula C of the present invention yielded very good results, with the aggregate scores of Formula C being about equal to those of Formula A, a prior art phosphorus formulation.

TABLE IV

EFFECT OF INHIBITOR SYSTEM ON SPOTTING AND FILMING

	Weight Percent Active Formula		
Ingredient	A	B	C
STPP	35.00	0	0
Sodium Carbonate	20.00	75.00	75.00
Sodium Sulfate	13.00	1.00	1.00
Sodium Silicate (SiO_2/Na_2O = 2.4)	12.23	8.00	8.00
Low-foam Surfactant	4.00	4.00	4.00
Sodium Dichloroisocyanurate	2.00	2.00	2.00
Sodium Polyacrylate (MW = 2730)	0	0	4.40
TIA	0	0	0.67
Water	13.77	10.00	4.93

Table III shows the effects of polycarboxylates and TIA's on washing efficacy with respect to four types of soils. Wash conditions include 30g of detergent added to the main wash, 120°F wash water and 125 ppm hardness (Ca/Mg = 3).

Table III

EFFECT OF INHIBITOR SYSTEM ON SOIL REMOVAL				
	Weight Percent Active Formula			
Ingredient	A	B	C	
STPP	35.00	0	0	
Sodium Carbonate	20.00	67.87	67.87	
Sodium Sulfate	13.00	0	0	
Sodium Silicate (SiO_2/Na_2O = 2.4)	12.23	8.00	8.00	
Low-foam Surfactant$^{(1)}$	4.00	4.00	4.00	
Sodium Dichloroisocyanurate	2.00	2.00	2.00	
Sodium Polyacrylate (MW = 2000)	0	0	6.16	
TIA$^{(2)}$	0	0	0.71	
Water	13.77	18.13	11.26	
Soil	Visual Grades			LSD_{95}
Starch	0.9	2.1	3.2	1.0
Oatmeal	8.5	7.9	8.3	0.9
Milk	6.7	7.9	7.4	1.3
Pudding	4.8	6.8	7.1	1.5
Average	5.2	6.2	6.5	0.8

Formula A = phosphorus-containing formula as control

Formula B = high carbonate without inhibitor system

Formula C = present invention

(1) Ethoxylated/propoxylated C_9 aliphatic alcohol
(2) Pentasodium 2-phosphonobutane-1,2,4-tricarboxylate

	Visual Grades (LSD_{95} = 0.8)		
Spotting	2.0	5$^{(a)}$	3.0
Filming	3.7	5$^{(a)}$	2.5

Formula A = phosphorus-containing composition as control

Formula B = high carbonate without inhibitor system

Formula C = present invention

(1) Ethoxylated/propoxylated C_a aliphatic alcohol
(2) 2-Phosphonobutane-1,2,4-tricarboxylate
(a) completely coated with calcium precipitates

Tables V-VII illustrate the effectiveness of the inhibitor system of the present invention as measured by turbidity of the detergent solutions. Turbidities were measured using a Hach 2100A turbidimeter, 30 minutes after detergent and hard water solutions were mixed to give 30 g of detergent in 7 L of water with hardnesses as indicated below. Results are shown in Nephelometric Turbidity Units (NTU).

V. SYNERGISM BETWEEN POLYMERS AND PHOSPHONATES

Example	Polymer wt% Type	Phosphonate wt% Type	Turbidity NTU
1	0	0.20 PBTC	160
2	0	0.20 HEDP	215
3	0	3.33 PBTC	80
4	0	3.40 HEDP	65
5	1.52 acrylic acid	0	85
6	1.52 acrylic acid	0.33 PBTC	50
7	1.52 acrylic acid	0.34 HEDP	55
8	1.52 acrylic acid	0.33 SHMP	60
Control(1)			20

HEDP = 1-Hydroxyethylidene-1,1-diphosphonic acid

PBTC = 2-Phosphonobutane-1,2,4-tricarboxylic acid

SHMP = Sodium hexametaphosphate

(1) Formula A, containing phosphorus

The formulas of Table V contain about 75% sodium carbonate, 8‰ sodium silicate (SiO_2/Na_2O = 2.4), 4% low-foaming surfactant, 2% dichloroisocyanurate, and water. The acrylic acid polymer had a weight average molecular weight of 2734 g/mole. Water hardness was 250 ppm as $CaCO_3$ (Ca/Mg = 3). All solutions were kept at 120° F in a heated water bath.

Examples 1-4 of Table V, without polyner, resulted in relatively high turbidities, indicating the presence of calcium precipitates. Example 5, having no TIA, similarly yielded a high turbidity, while Examples 6-9 resulted in acceptably low turbidities.

Table VI shows the effect of various types and amounts of polycarboxylic acid polymer and of TIA on calcium precipitation in hard (400ppm) water. Generally, lower turbidities reflect fewer calcium precipitates.

VI. EFFECT OF INHIBITOR SYSTEM AND CARBONATE LEVELS ON TURBIDITY

No.	Na_2CO_3 wt%	Polymer wt%	TIA wt% Type	Turbidity NTU
1	75.0	1.60 AA	1.08 PBTC	100
2	75.0	2.14 AA	0.50 PBTC	115
3	75.0	2.14 AA	1.67 PBTC	64
4	75.0	3.43 AA	0.27 PBTC	66
5	75.0	3.43 AA	1.08 PBTC	46
6	75.0	3.43 AA	1.90 PBTC	33
7	75.0	4.73 AA	0.25 PBTC	47

VI. EFFECT OF INHIBITOR SYSTEM AND CARBONATE LEVELS ON TURBIDITY (cont.)

	Na_2CO_3	Polymer		TIA		Turbidity
No.	wt%	wt%		wt%	Type	NTU
8	75.0	4.73	AA	0.38	PBTC	39
9	75.0	4.73	AA	0.50	PBTC	34
10	75.0	4.73	AA	1.67	PBTC	29
11	75.0	5.26	AA	1.08	PBTC	23
12	75.0	4.73	AA	1.00	SHMP	36
13	75.0	4.73	AA	3.33	SHMP	31
14	75.0	5.26	AA	2.17	SHMP	28
15	67.9	6.17	NaA	0.50	PBTC	20
16	67.9	6.17	NaA	0.50	HEDP	26
17	67.9	6.17	NaA	0.50	ATMP	22
18	67.9	4.01	NaA	0.50	PBTC	34
19	67.9	4.01	NaA	0.80	HEDP	36
20	67.9	4.01	NaA	0.80	ATMP	34
21	75.0	3.97	AA*	0.67	PBTC	115
22	75.0	4.29	NaA$^{(1)}$	0.67	PBTC	64
23	75.0	4.22	NaA$^{(2)}$	0.67	PBTC	93
24	75.0	4.17	NaA$^{(3)}$	0.67	PBTC	110
25	75.0	4.17	NaA/MA$^{(4)}$	0.67	PBTC	80
26	75.0	4.17	NaA/NaM$^{(5)}$	0.67	PBTC	93
27	75.0	4.17	NaA/NaM$^{(6)}$	0.67	PBTC	94
28	75.0	4.17	NaMA$^{(7)}$	0.67	PBTC	97
29	75.0	4.17	NaMA$^{(8)}$	0.67	PBTC	85
30	75.0	4.17	MVE/MA	0.67	PBTC	99
31	Control$^{(10)}$					24

ATMP = Aminotri(methylene phosphonic acid)
HEDP = 1-Hydroxyethylidene-1,1-diphosphonic acid
PBTC = 2-Phosphonobutane-1,2,4-tricarboxylic acid
SHMP = Sodium hexametaphosphate
AA = Acrylic Acid, MW = 2,000 g/mole
AA* = Acrylic Acid, MW = 1,000 g/mole

NaA = Sodium acrylate, MW = 4,500 g/mole
MA = Methylacrylate
NaMA = Sodium methacrylate
NaM = Sodium maleate
MVE/MA = Methyl vinyl ether/Maleic Acid, MW = 20,000 g/mole
(1) MW = 2,100 g/mole
(2) MW = 5,800 g/mole
(3) MW = 10,000 g/mole
(4) MW = 3,000 g/mole
(5) MW = 20,000 g/mole
(6) MW = 50,000 g/mole
(7) MW = 2,000 g/mole
(8) MW = 4,500 g/mole

(10) Formula A, containing phosphorus

The formulas of Table VI, above, also contain about 8% sodium silicate (SiO_2/Na_2O = 2.4), 4% low-foaming surfactant, 2% dichloroisocyanurate, and water. Water hardness was 400 ppm as $CaCO_3$ (Ca/Mg = 3). All solutions were kept at 140° F in a heated water bath.

VII. EFFECT OF POLMER MOLECULAR WEIGHT ON TURBIDITY

No.	Na_2CO_3 wt%	Polymer wt%	MW (g/mole)	Phosphonate wt% Type	Turbidity NTU
1	67.9	6.17 NaA	2000	0.50 PBTC	31
2	67.9	6.10 NaA	2100	0.50 PBTC	27
3	67.9	6.17 NaA	3680	0.50 PBTC	34
4	67.9	6.17 NaA	4500	0.50 PBTC	26
5	67.9	6.15 NaA	5100	0.50 PBTC	26
6	67.9	6.25 NaA	5800	0.50 PBTC	28
7	67.9	6.17 NaA	20000	0.50 PBTC	47
8	Control(1)				24

(1) Formula A, containing phosphorus

Table VII exemplifies an appropriate molecular weight range of effectiveness of the polymers herein. It can be seen that acceptable turbidities result from the use of sodium polyacrylate with a molecular weight range of about 2000-5800. At a molecular weight of 20,000, however, the turbidity increases, indicating observable calcium precipitation.

While described in terms of the presently preferred embodiments, it is to be understood that such disclosure is not to be interpreted as limiting. Various modifications and alterations will no doubt occur to those skilled in the art after having read the above disclosure. Accordingly, it is intended that the appended claims be interpreted as covering all alterations and modifications as fall within the true spirit and scope of the invention.

Claims

1. A dry detergent composition for use in an automatic dishwasher comprising

(a) about 30-80% builder consisting essentially of an alkali-metal carbonate;

(b) about 2-30% of an alkali-metal silicate, having a SiO_2/M_2O ratio of between about 1-4;

(c) a low foaming surfactant; and

(d) a calcium crystal growth-inhibiting amount of an inhibitor system, including at least a polycarboxylic acid, and a threshold inhibiting agent selected from the group consisting of monomeric phosphonate-containing organic compounds, inorganic oligomeric phosphates, and mixtures thereof.

2. A composition as claimed in claim 1 characterised in that
the low-foaming surfactant is selected from alkoxylated aliphatic alcohols, alkoxylated alkyl phenols, copolymers of C_{1-4} alkylene oxides and mixtures thereof.

3. A composition as claimed in claim 1 or claim 2 characterised in that
the surfactant is an ethoxylated/propoxylated aliphatic alcohol.

4. A composition as claimed in any of claims 1 to 3 characterised in that
it further includes a bleaching-effective amount of a bleach.

5. A composition as claimed in any of claims 1 to 4 characterised in that
the alkali-metal carbonate is present in an amount of at least 40% by weight.

6. A composition as claimed in any of claims 1 to 5 characterised in that
the alkali-metal carbonate is sodium carbonate; the alkali-metal silicate is sodium silicate; the polycarboxylic acid is polyacrylic or polymethacrylic acid having a molecular weight of between about 1000-10,000 g/mole; and the threshold inhibiting agent is selected from the group consisting of poly phosphonates/carboxylates of mono-, di-, and tri-alkylamines having at least one phosphonate group; 1-hydroxyethylidene-1,1-diphosphonic acid, aminotri-(methylenephosphonic acid) ; sodium hexametaphosphate; 2-phosphonobutane-1,2,4-tricarboxylic acid; phosphonohydroxy acetic acid; and mixtures thereof.

7. A composition as claimed in any of claims 1 to 6 characterised in that
the TIA is selected from the group consisting of ATMP, PBTC, HEDP, SHMP and mixtures thereof.

8. An automatic dishwashing detergent composition consisting essentially of

(a) about 30-80% of a builder consisting essentially of sodium carbonate;

(b) about 2-30% of a sodium silicate having a SiO_2/M_2O ratio of about 1-4;

(c) about 0.1-10% of a polyacrylic acid having a molecular weight of between about 1,000 and 10,000 g/mole;

(d) about 0.1-5% of a threshold inhibiting agent selected from the group consisting of monomeric phosphonate-containing organic compounds, inorganic oligomeric phosphates, and mixtures thereof;

(e) a low-foaming surfactant; and

(f) a bleaching-effective amount of a bleaching species.

9. A composition as claimed in claim 8 characterised in that
the threshold inhibiting agent is selected from the group consisting of poly phosphonates/carboxylates of mono-, di-, and tri-alkylamines having at least one phosphonate group; 1-hydroxyethylidene-1, 1-diphosphonic acid, aminotri-(methylenephosphonic acid) ; sodium hexametaphosphate; 2-phosphonobutane-1,2,4-tricarboxylic acid; phosphonohydroxy acetic acid; and mixtures thereof.

10. A composition as claimed in claim 8 or claim 9 characterised in that
the alkali-metal carbonate is present in an amount of at least 40% by weight.

11. A composition as claimed in any of claims 8 to 10 characterised in that
the low-foaming surfactant is selected from the group consisting of alkoxylated aliphatic alcohols, alkoxylated alkyl phenols, copolymers of C_{1-4} alkylene oxides and mixtures thereof.

12. A method of washing wares comprising
contacting the wares with a cleaning effective amount of a detergent composition as claimed in any of claims 1 to 11 in aqueous solution.

13. A method for washing wares comprising
contacting the wares with a cleaning effective amount of a detergent composition, in aqueous solution, comprising

(a) about 30-80% builder consisting essentially of an alkali-metal carbonate;

(b) about 2-30% of an alkali-metal silicate with a SiO_2/M_2O ratio of about 1-4;

(c) about 0.-10% of a polyacrylic acid having a molecular weight of between about 1,000 and 10,000 g/mole;

(d) about 0.5-5% of a TIA selected from the group consisting of monomeric phosphonate-containing organic compounds, inorganic phosphates, and mixtures thereof;

(e) about 0-2% of a bleach; and

(f) about 0-5% of a low-foaming nonionic surfactant.

14. A method as claimed in claim 12 or claim 13 characterised in that
the threshold inhibiting agent is selected from the group consisting of poly phosphonates/carboxylates of mono-, di-, and tri-alkylamines having at least one phosphonate group; 1-hydroxyethylidene-1, 1-diphosphonic acid, aminotri-(methylenephosphonic acid) ; sodium hexametaphosphate; 2-phosphonobutane-1,2,4-tricarboxylic acid; phosphonohydroxy acetic acid; and mixtures thereof.

15. A method as claimed in any of claims 12 to 14 characterised in that
the alkali-metal carbonate is present in an amount of at least 40% by weight.

16. A method as claimed in any of claims 12 to 15 characterised in that
the low-foaming surfactant is selected from the group consisting of alkoxylated aliphatic alcohols, alkoxylated alkyl phenols, copolymers of C_{1-4} alkylene oxides and mixtures thereof.