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NL-2587 BP 's-Gravenhage(NL)(54) **Automatic dishwasher detergent composition containing dual bleach system.**

(57) The application is directed to an automatic dishwasher detergent powder composition containing a dual bleach system. The composition contains a chlorine bleach source and a bromide compound. In the wash bath the chlorine source reacts with water to form hypochlorite and the bromide compound reacts with a portion of the hypochlorite to form hypobromite. The active ingredients of the dual bleach system are the hypochlorite and hypobromite which provide improved cleaning performance against both proteinaceous and starchy carbohydrate soils. The powder compositions are dry, free flowing, readily dispersed and easily soluble in the wash bath.

EP 0 395 186 A2

AUTOMATIC DISHWASHER DETERGENT COMPOSITION CONTAINING DUAL BLEACH SYSTEMFIELD OF THE INVENTION

5 The present invention relates to an automatic dishwasher detergent composition having improved cleaning performance against difficult to remove soils. The present invention is more particularly directed to a stable dry powder detergent composition containing a dual bleach system for use in an automatic dishwasher to clean dishware, glassware, cookware and the like.

The present invention also relates to an improved powder composition and to a method of making and using the composition.

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BRIEF DESCRIPTION OF THE INVENTION

15 The present invention is directed to an automatic dishwasher detergent composition having improved cleaning performance for proteinaceous and carbohydrate soils. The detergent composition contains a chlorine bleach source and a bromide source. The detergent composition more particularly contains a source of hypochlorite ion and a source of bromide ion.

When the detergent composition is added to a wash bath a portion of the hypochlorite ion reacts in situ with the bromide ion to form hypobromite ion which is a powerful oxidizing agent.

20 The newly formed hypobromite ion is an effective agent for cleaning carbohydrate soils and the remaining unreacted hypochlorite ion is an effective agent for cleaning proteinaceous soils.

The present invention specifically relates to automatic dishwashing detergent powder compositions having improved cleaning performance against proteinaceous and starchy carbohydrate soils on dishware, glassware, cookware and the like, particularly cooked on and baked on soils.

25 The powder compositions are dry, free flowing, readily dispersed and easily soluble in the wash bath.

PRIOR ART

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Commercially available household-machine dishwasher detergents provided in powder or liquid form have the disadvantage of not being effective in cleaning both proteinaceous and starchy carbohydrate soils. The cooked on and baked on proteinaceous and starchy carbohydrate soils are particularly hard to remove. 35 Though some detergent compositions have been found to be effective in removing proteinaceous soils and others have been found effective in removing starchy carbohydrate soils, none have been found effective in removing both proteinaceous and starchy carbohydrate soils from dishware, glassware, cookware and the like.

For effective use, it is generally recommended that the automatic dishwashing detergent, hereinafter also designated ADD, contain (1) sodium tripolyphosphate (NaTPP) to soften or tie up hard-water minerals and to emulsify and/or peptize soil; (2) sodium silicate to supply the alkalinity necessary for effective detergency and to provide protection for dishware, such as fine china and protection against machine corrosion; (3) sodium carbonate, generally considered to be optional, to enhance alkalinity; (4) a chlorine-releasing agent to aid in cleaning; (5) a surfactant and (6) a defoamer to reduce foam, thereby enhancing machine efficiency. See, for example, SDA Detergents in Depth, "Formulations Aspects Of Machine Dishwashing," Thomas Oberle (1974). Cleansers approximating to the afore-described compositions are mostly liquids or powders. Generally, such compositions omit hypochlorite bleach, since it tends to react with other chemically active ingredients, particularly surfactant, thereby impairing its effectiveness.

40 The most difficult food soils to remove from dishware, cookware and utensils are proteinaceous and starchy carbohydrate soils. The proteinaceous soils can be in the form of baked on or cooked on milk, meats and egg soils. The starchy carbohydrate soils can be in the form of baked on or cooked on starchy carbohydrates such as pasta, oatmeal, porridge, bread, cake and the like.

50 These two types of food soils are very tenaciously bound to the dishware, cookware and utensil substrates and are very difficult to clean without scrubbing.

Proteinaceous materials, for example, egg protein can be removed by appropriate concentrations of, for

example, sodium hypochlorite bleach. However, dishwasher detergent compositions containing hypochlorite ion perform poorly on starchy carbohydrate soils.

The hypobromite ion is a strong oxidizing agent, but is so reactive that it is chemically unstable in detergent compositions. Bromide ion when contacted with hypochlorite in an aqueous alkaline medium reacts to form hypobromite. The hypobromite effectively degrades starchy carbohydrates.

However, if too much bromide ion is present in the wash bath, it will substantially reduce the hypochlorite ion concentration and/or will completely remove the hypochlorite from the wash bath and the proteinaceous soils are not removed.

If an insufficient amount of bromide ion is present the starchy carbohydrate soils are not removed.

The problem to be solved was to formulate a dishwasher detergent composition that was stable in storage and was effective in a wash bath in removing both proteinaceous and starchy carbohydrate soils.

In the Diez USP 3,519,569 there is disclosed an abrasive scouring cleaner containing as essential ingredients a water soluble siliceous abrasive material, a hypochlorite-chlorine liberating compound, a water soluble detergent compound and an alkali metal bromide.

The Finck USP 4,102,799 discloses an alkaline automatic dishwasher detergent composition which is essentially free of inorganic phosphates and which consists essentially of a citrate compound, and one or more inorganic builder salts such as silicates, carbonates and/or sulfate. The composition can also contain one or more bleaching agents which are capable of liberating hypochlorite chlorine and/or hypobromite bromine on contact with aqueous media.

The Hartman European Patent Application No. 0,186,234 discloses an automatic dishwasher powder detergent composition comprising a detergent builder, a source of hypochlorite, a low-sudsing nonionic surfactant, an anti-sudsing agent and an alkali metal or alkaline earth metal bromide.

ADVANTAGES OVER THE PRIOR ART

The detergent compositions of the present invention overcome many of the prior art problems. Because of the addition of a small effective amount of a bromide to the compositions, which generates hypobromite in the wash bath the composition can be used to remove both proteinaceous and starchy carbohydrate soils from dishware, glassware, cookware and the like. The detergent composition has the additional advantages of being stable in storage and readily redispersible in the dishwashing machines. The powder compositions of the present invention are easily pourable, easily measured and easily put into the dishwashing machines.

In accordance with the present invention a stable powder dishwashing detergent composition containing a balanced source of hypochlorite ion and hypobromite ion is advantageously provided such that the composition efficiently and effectively cleans both proteinaceous and starchy carbohydrate soils from dishware, glassware, cookware and utensils in an automatic dishwashing machine.

The powder detergent compositions of the present invention are stable in storage, and readily dispersed and easily soluble in the washing machine.

OBJECTS OF THE PRESENT INVENTION

It is an object of the present invention to provide an automatic dishwasher detergent composition that has improved cleaning performance against difficult to remove proteinaceous and starchy carbohydrate soils.

It is another object of the invention to provide a powder detergent composition which is stable in storage, does not degrade or decompose, is readily dispersible and is easily soluble in the dishwashing water.

Another object of the present invention is to prepare an automatic dishwasher detergent composition which contains both a chlorine bleach source and a bromide source.

Another object of the present invention is to prepare an automatic dishwasher detergent composition which on addition to a wash bath generates a balanced amount of hypochlorite ions and hypobromite ions which are strong oxidizing agents and together are effective in cleaning both proteinaceous and starchy carbohydrate soils.

A further object of the invention is to provide a method of washing dishware, glassware, cookware and the like in an automatic dishwashing machine using a dual bleach system detergent composition which is

effective in removing both proteinaceous and starchy carbohydrate soils.

A still further object of the invention is to provide a method of washing dishware, glassware, cookware and the like in an automatic washing machine using a powder detergent composition by which method both proteinaceous and starchy carbohydrate soils are efficiently and effectively removed from dishware, glassware, cookware and the like.

It is a further object of this invention to provide stable dry powder detergent dual bleach compositions, especially automatic dishwasher detergent compositions, by incorporating in the compositions a source of chlorine bleach and a small effective amount of bromide compound.

DETAILED DESCRIPTION OF THE INVENTION

These and other objects of the invention which will become more readily understood from the following detailed description of the invention and preferred embodiments thereof are achieved by incorporating in the detergent composition a source of chlorine bleach and a small but effective amount of bromide as the dual bleach system.

In accordance with the present invention there is provided a dry powder automatic dishwasher detergent composition which includes, on a weight basis;

- (a) 20 to 70% organic or inorganic builder salt;
- (b) 5 to 40% sodium silicate;
- (c) chlorine bleach compound in an amount to provide 0.5 to 5% available chlorine;
- (d) 0.1 to 2.0% bromide compound;
- (e) 0 to 15% alkali metal carbonate;
- (f) 0.1 to 6% chlorine bleach stable, water dispersible organic detergent active material;
- (g) 0 to 6% chlorine bleach stable foam depressant; and
- (h) 0-30% sodium sulfate.

The mole ratio of the bromide to available chlorine is critical and is 0.04 to 0.12.

The present invention also provides a method for cleaning dishware, glassware and cookware in an automatic dishwashing machine with an aqueous wash bath containing an effective amount of the automatic dishwasher detergent (ADD) powder composition as described above. According to this aspect of the invention, the ADD composition is dry free flowing powder and can be readily poured into the dispensing cup of the automatic dishwashing machine and will remain within the dispensing cup until subjected to the water spray from the dishwashing machine.

The invention will now be described in greater detail by way of specific embodiments thereof.

In accordance with the present invention an improved automatic dishwasher detergent composition is prepared by incorporating small amounts of a bromide containing compound in a dishwasher composition containing a source of hypochlorite ion. When the composition is added to a dishwasher wash bath the bromide reacts with a portion of the hypochlorite and the bromide is converted to hypobromite, a strong oxidizing agent.

The present invention is based upon the surprising and unexpected discovery that substantially improved cleaning performance for both proteinaceous and starchy carbohydrate soils can be obtained by adding to an aqueous liquid detergent composition a source of hypochlorite and a small effective amount of a bromide compound which when added to the wash bath form a hypochlorite and hypobromite dual bleach system.

CHLORINE BLEACH COMPOUND

Hypochlorite generating compounds suitable for use in the compositions of the present invention are those water soluble dry solid materials which generate hypochlorite ion on contact with, or dissolution in, water. Examples thereof are the dry, particulate heterocyclic N-chlorimides such as trichlorocyanuric acid, dichlorocyanuric acid and salts thereof such as sodium dichlorocyanurate and potassium dichlorocyanurate. The corresponding dichloroisocyanuric and trichloroisocyanuric acid salts can also be used. Other N-chloroimides may be used such as N-chlorosuccinimide, N-chloromalonimide, N-chlorophthalimide and N-chloronaphthalimide. Additional suitable N-chloroimides are the hydantoins such as 1,3-dichloro-5,5-dimethylhydantoin;

N-monochloro-C,C-dimethylhydantoin;
 methylene-bis (N-chloro-C,C-dimethylhydantoin);
 1,3-dichloro-5-methyl-5-isobutylhydantoin;
 1,3-dichloro-5-methyl-5-ethylhydantoin;
 1,3-dichloro-5,5-diisobutylhydantoin;
 1,3-dichloro-5-methyl-5-n-amyhydantoin;

and the like. Other useful hypochlorite-liberating agents are trichloromelamine and dry, particulate, water soluble anhydrous inorganic salts such as lithium hypochlorite. The hypochlorite liberating agent may, if desired, be a stable, solid complex or hydrate such as sodium p-toluene-sulfo-chloramine-trihydrate (chloramine-T), sodium benzene-sulfo-chloramine-dihydrate, calcium hypochlorite tetrahydrate, or chlorinated trisodium phosphate containing 0.5 to 4% available chlorine produced by combining trisodium phosphate in its normal $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ form and an alkali metal hypochlorite (e.g., sodium hypochlorite).

The preferred sources of hypochlorite are dichloro- and trichloroisocyanurates, lithium hypochlorite, calcium hypochlorite and chloramine-T (p-Toluenesulfochloramine).

Typically the instant chlorine-liberating agents are employed in a proportion of about 1 to 15% by weight of the composition, and preferably about 1.0 to 10% and more preferably 2 to 6.5%. Desirably the proportion thereof employed will be such as to yield a product which contains from about 0.5% to about 5% available chlorine on a total weight basis, preferably 1 to 4% and more preferably 1 to 3.5% available chlorine.

The composition should contain sufficient chlorine bleach compound to provide about 0.5 to 5.0% by weight of available chlorine, as determined, for example, by acidification of the composition with sulfuric acid and iodometric titration with sodium thiosulfate monitored by a potentiometer. A composition containing about 0.9 to 9% by weight of sodium dichloroisocyanurate dihydrate contains or provides about 0.5 to 5% available chlorine. A composition containing about 1.8 to 5.4% by weight sodium dichloroisocyanurate dihydrate contains about 1 to 3% by weight of available chlorine and is especially preferred. A composition containing about 1.6 to 4.8% by weight calcium hypochlorite contains about 1 to 3% by weight available chlorine.

BROMIDE COMPOUND

The bromide source or compound used in the present invention is a solid water soluble bromide which preferably is of substantially neutral or slightly alkaline nature, providing a ready source of bromide ions on dissolution in water. It is preferred to employ alkali metal bromides such as sodium bromide, sodium bromide dihydrate, lithium bromide, and potassium bromide, although alkaline earth metal bromides such as calcium bromide and magnesium bromide may be employed in those instances in which these water hardness-producing cations are not objectionable.

The bromide compound for example alkali metal bromides are used in amounts of 0.1 to 3 wt.%, preferably 0.2 to 2.0 wt.% and more preferably 0.3 to 1.5 wt.%.

Preferably the bromide is employed in an amount which is substantially less than the molar equivalent of available chlorine present in the product, e.g., the mole ratio of water soluble bromide to available chlorine is in the range of 0.04 to 0.12, preferably less than 0.10, for example 0.05 to 0.95, and typically 0.05 to 0.090.

A balanced detergent composition is obtained which contains a small effective amount of the bromide to react with the hypochlorite to form a sufficient amount of hypobromite to remove the starchy carbohydrate soil and to leave a sufficient amount of hypochlorite ion in the wash bath to remove the proteinaceous soil.

Thus, the weight percent available chlorine and the mole ratio of bromide to available chlorine are critical features of the present invention.

BUILDER SALTS

Generally, ADD effectiveness is directly related to (a) available chlorine levels; (b) alkalinity; (c) solubility in washing medium; and (d) foam inhibition. It is preferred herein that the pH of the ADD composition be at least about 9.5, more preferably from about 10.5 to 13.5 and most preferably at least about 11.5.

The amount of alkali metal silicate added and the amount of alkali metal TPP added can be used to obtain the desired alkalinity. The sodium carbonate can be added to act as a buffer to maintain the desired pH level. the sodium carbonate can be added in an amount of 0 to 30 wt.%, preferably 5 to 25 wt.% and typically about 10 to 20 wt.% of the detergent composition.

5 The compositions of the present invention can contain inorganic builder salts such as NaTPP or organic builder salts such as the alkali metal salts of citric and tartaric acid.

A preferred solid builder salt is an alkali metal polyphosphate such as sodium tripolyphosphate ("TPP"). In place of all or part of the alkali metal polyphosphate one or more other detergent builder salts can be used. Suitable other builder salts are alkali metal borates, phosphates and bicarbonates.

10 Specific examples of such builders are sodium tetraborate, sodium pyrophosphate, potassium pyrophosphate, sodium bicarbonate, sodium hexametaphosphate, sodium sesquicarbonate, sodium mono and diorthophosphate and potassium bicarbonate.

The NaTPP may be employed in the ADD composition in a range of 5 to 70%, preferably about 10 to 65 wt.%, and more preferably about 20 to 60 wt.%, and should preferably be free of heavy metal which tends to decompose or inactivate the chlorine bleach compounds. The NaTPP may be anhydrous or hydrated, including the stable hexahydrate with a degree of hydration of 6 corresponding to about 18% by weight of water or more.

Especially preferred ADD compositions are obtained, for example, when using a 0.5:1 to 2:1 weight ratio of anhydrous to hexahydrated NaTPP, values of about 1:1 being particularly preferred.

20 The NaTPP may be replaced in whole or in part by organic builder salts.

Since the compositions of this invention are generally highly concentrated, and, therefore, may be used at relatively low dosages, it is desirable to supplement any phosphate builder (such as sodium tripolyphosphate) with an auxiliary builder such as an alkali metal polycarboxylic acid. Suitable alkali metal polycarboxylic acids are alkali metal salts of citric and tartaric acid, e.g. monosodium and disodium citrate (anhydrous). The sodium salts of citric and tartaric acids are preferred.

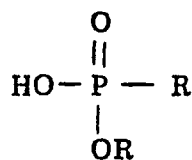
Alkali metal sulfates, preferably sodium sulfate is added as an anhydrous filler material. The sodium sulfate can be added in an amount of 0-30%, preferably 5 to 25%, and more preferably 15 to 20% by weight of the composition.

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Foam Inhibitors

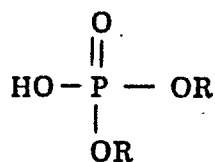
Foam inhibition is important to increase dishwasher machine efficiency and minimize destabilizing effects which might occur due to the presence of excess foam within the washer during use. Foam may be sufficiently reduced by suitable selection of the type and/or amount of detergent active material, the main foam-producing component. The degree of foam is also somewhat dependent on the hardness of the wash water in the machine whereby suitable adjustment of the proportions of NaTPP 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

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

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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_{12-20} alkyl group. 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_{16-18} alkyl acid phosphate esters such as monostearyl/distearyl acid phosphates 1.2/1 (Knapsack). When employed, proportions of 0.01 to 5 wt.%, preferably 0.1 to 5 wt.%, especially about 0.1 to 0.5 wt.%, of foam depressant in the composition is typical, the weight ratio of detergent active component to foam depressant 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.

The sodium silicate, which provides alkalinity and protection of hard surfaces, such as fine china, is employed in an amount ranging from about 5 to 40 wt.%, preferably about 8 to 35 wt.%, and more preferably about 10 to 25 wt.%, in the composition. The sodium silicate also protects the washing machine from corrosion. The sodium silicate can have a $NaO:SiO_2$ ratio of 1.6/1 to 1/3.2. The sodium silicate can be added in the form of an aqueous solution, preferably having an $Na_2O:SiO_2$ ratio of from 1/1 to 1/2.8, for example, 1/2.4. Potassium silicates of the same ratios can also be used. The preferred alkali metal silicates are sodium disilicate and sodium metasilicate.

Most of the other components of the composition, especially calcium hypochlorite and foam depressant can be added in the form of dry powders or aqueous dispersions or solutions.

Liquid Nonionic Surfactant Detergents

The liquid nonionic surfactant detergents that can be used in the practice of the present are preferably the low foam poly-lower alkoxyated lipophiles.

The nonionic synthetic organic detergents are 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 (hydrophilic in nature). The length of the hydrophilic or polyoxy ethylene chain can be readily adjusted to achieve the desired balance between the hydrophobic and hydrophilic groups.

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 alkoxyated higher alkanol wherein the alkanol is of 9 to 18 carbon atoms and wherein the number of mols of lower alkylene oxide (of 2 or 3 carbon atoms) is from 3 to 12. Of such materials it is preferred to employ those wherein the higher alkanol is a higher 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 mol. Preferably, the lower alkoxy is ethoxy but in some instances, it may be desirably mixed with propoxy, the latter, if present, usually being a minor (less than 60%) proportion. Exemplary of such compounds are those wherein the alkanol is of 12 to 15 carbon atoms and which contain about 7 ethylene oxide groups per mol.

Useful nonionics are represented by the low foam 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 moles propylene oxide and 4 moles ethylene oxide and a $C_{13}-C_{15}$ fatty alcohol condensed with 5 moles propylene oxide and 10 moles ethylene oxide. Another group of low foam liquid nonionics are available from Shell Chemical Company, Inc. under the Dobanol trademark: Dobanol 91-5 is a low foam ethoxylated C_9-C_{11} fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated $C_{12}-C_{15}$ fatty alcohol with an average of 7 moles ethylene oxide.

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

A preferred nonionic surfactant is available from Union Carbide Corporation under the trademark Tergitol MDS-42. This nonionic surfactant is a $C_{12}-C_{14}$ linear alcohol containing 55% by weight random

distributed oxyalkyl groups of which 42% are ethoxy and 58% propoxy groups.

Other useful nonionic surfactants are the Poly-Tergent S-LF surfactants available from Olin Corporation. These surfactants are low foaming, biodegradable linear fatty alcohols. Surfactants of this type are available under the tradenames Poly-Tergent S-LF 18, Poly-Tergent S-305-LF, Poly-Tergent, S-405-LF and poly-Tergent CS-1.

Also useful in the present compositions as a component of the nonionic detergent 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 mol being about 11. Such products are also made by Shell Chemical Company.

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 detergent active materials used herein must be stable in the presence of chlorine bleach, especially hypochlorite bleach. In addition to the above discussed nonionic surfactants, anionic surfactants can also be used.

The anionic surfactants that can be used are the linear or branched alkali metal mono- and/or di-(C₈₋₁₄) alkyl diphenyl oxide mono and/or disulphonates, commercially available for example as DOWFAX (Registered Trademark) 3B-2 and DOWFAX 2A-1.

Other suitable surfactants include the primary alkylsulphates, alkylsulphonates, alkylaryl-sulphates and sec. alkylsulphates. Examples include sodium C₁₀₋₁₈ alkylsulphates such as sodium dodecylsulphate and sodium tallow alcoholsulphate; sodium C₁₀₋₁₈ alkanesulphonates such as sodium hexadecyl-1-sulphonate and sodium C₁₂₋₁₈ alkylbenzenesulphonates such as sodium dodecylbenzenesulphonates. The corresponding potassium salts may also be employed.

The nonionic and anionic surfactants are used in amounts of 0.1 to 6%, for example about 0.5 to 5.5%, preferably about 1.0 to 5.0%.

Various conventional ingredients may be included in these compositions in small amounts, generally less than about 4 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 compound and high alkalinity (properties of all the components). Especially preferred for coloring are the chlorinated phthalocyanines and polysulphides of aluminosilicate which provide, respectively, pleasing green and blue tints.

The powder ADD compositions of this invention are readily employed in known manner for washing dishes, glasses, cups, cookware, eating 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.

In an embodiment of the invention a regular strength automatic dishwashing detergent composition is formulated using the below named ingredients.

Regular Strength		
Component	Weight Percent	Preferred Weight Percent
Sodium Tripolyphosphate	25-45	30-40
Sodium Carbonate	5-25	15-20
Sodium Sulfate	5-25	15-20
Nonionic Surfactant	1-4	2-4
Sodium Silicate	8-20	10-15
Sodium Bromide	0.20 to 1.0	0.30 to 0.60
Sodium Dichloroisocyanurate	1 to 4	1.5 to 3.0
Color, Perfume	0.5 to 2.5	1 to 2
Moisture	2-12	4-8

In another embodiment of the invention concentrated heavy duty powder automatic dishwasher detergent powder composition is formulated using the below named ingredients.

Concentrated Heavy Duty		
Component	Weight Percent	Preferred Weight Percent
Sodium Tripolyphosphate	55-65	58-62
Sodium Carbonate	-	-
Sodium Sulfate	-	-
Nonionic Surfactant	2 to 6	3 to 5
Sodium Silicate	15-35	18-25
Sodium Bromide	0.30 to 2.0	0.50 to 1.5
Sodium Dichloroisocyanurate	2 to 8	4 to 6.5
Color, Perfume	1-3.5	2-3
Moisture	2-12	4-8

The dishwasher detergent compositions of the present invention can contain conventional dishwashing detergent composition additives. The formulations can be prepared with commercially available powder builders, chlorine bleach source compounds and bromide compounds.

The formulations can be prepared using the conventional dry blending and agglomeration procedures used for the preparation of dry powder detergent compositions.

In dry the blending procedure, nonionic surfactant is thoroughly mixed with STPP by overspraying it at 120° F in a twin-shelled mixer. The STPP beads containing absorbed surfactant are then conditioned, that is allowed to sit overnight. The loaded STPP material is then successively mixed with sodium bromide, sodium carbonate, sodium sulfate and sodium silicate granules. Finally sodium dichloroisocyanurate is added and blended with the rest and mixed thoroughly in the mixer.

A preferred method for preparing the automatic dishwasher detergent powder compositions of the present invention is the agglomeration procedure which is briefly discussed below. The agglomeration procedure provides better bleach stability of coating the nonionic surfactant with the sodium silicate which separates the nonionic surfactant from the reactive bleach.

In accordance with the agglomeration procedure, about half of the STPP builder salt in the form of powder granules is introduced into a rotary drum and sprayed with the nonionic liquid surfactant at a temperature of about 120° F. The STPP granules during the spraying operation are maintained at a temperature of about 100° F.

The STPP granules loaded with the nonionic surfactant are dried overnight. The loaded dried STPP is mixed with the remaining STPP, sodium bromide, sodium carbonate and sodium sulfate in an agglomerator.

An aqueous solution of sodium silicate is then sprayed on the mixed powders in the agglomerator.

The mixed agglomerated powders are then added to a granulator in order to sieve out the desired particle size of the agglomerate. From the granulator the powder composition is fed to a fluid bed drying unit to dry the powder. Finally, sodium dichloroisocyanurate is post added and blended with agglomerated granules to complete the process.

One or more ingredients can be omitted or additional ingredients such as perfumes and anti-foam agents can be added to the composition.

The order of adding the solid powder ingredients to the agglomerator is not particularly critical as long as good mixing is achieved.

The term dry powder compositions as used herein is intended to include free flowing powder compositions containing 0-15% moisture, typically 2-12% and more typically 4-8% moisture. The moisture can be present in the form of hydrated compounds, for example, sodium tripolyphosphate hexahydrate, hydrated sodium carbonate, hydrated sodium sulfate and dichloroisocyanurate dihydrate and/or in the form of water.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

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

The present invention is further illustrated by the following examples.

Example 1

In accordance with the present invention automatic dishwasher powder detergent compositions are formulated following the above discussed procedure using the below named ingredients in the amounts indicated.

Ingredient	Regular Powder	Concentrated Powder	Prior Art Cascade Powder
Sodium Tripolyphosphate	34.8%	60.0%	35.3%
Sodium Carbonate	19.0%	-	20.0%
Sodium Sulfate	19.0%	-	18.0%
Nonionic Surfactant	3.0% ⁽¹⁾	4.0% ⁽¹⁾	3.5%
Sodium Silicate (1:2.4)	12.0%	22.0%	10.0%
Sodium Bromide	0.40	0.80	
Sodium Dichloroisocyanurate	2.68% ⁽²⁾	5.36% ⁽²⁾	1.8%
Color, Perfume	—	—	—
Moisture	—	—	—

(1) Tergitol MDS-42, from Union Carbide Corporation.

ACI 56, 56% available chlorine, available from Monsanto Corporation.

The mole ratio of bromide to available chlorine in the regular power composition is about 0.09 and the mole ratio of the bromide to available chlorine in the concentrated powder is about 0.09.

Multi-soil cleaning tests are run at stress conditions of 120° F wash cycle temperature and 300 ppm hard water in a low performance dishwasher. This is done to show differences between the products which are less apparent in normal use conditions with tap water and 140° F wash temperature.

Egg soil is prepared by mixing egg yolk with an equal amount of 2.5N calcium chloride solution. 0.4 grams of this mixture is applied to the usable surface of 7.5 inch china plates in a thin film. The plates are aged in 50% relative humidity overnight.

Oatmeal soil is prepared by boiling 24 grams of Quaker Oates in 400 ml of tap water for ten minutes. 3 grams of this mixture is spread onto a 7.5 inch china plate. The plates are aged for 2 hours at 80° C. They are then stored overnight at room temperature. Two plates are used per wash.

The plates are always placed in the same position in the dishwasher.

The detergent products to be tested are added at the beginning of the wash cycle. All plates are scored by measuring the percent area cleaned.

The multi-soil cleaning test results are reported below:

Product	Percent Soil Removal	
	Egg	Starch
Cascade Powder	2.8	28
Regular Powder	5.4	80
Concentrated Powder	8.0	52

The above compositions are also tested cleaning glass tumblers.

The ASTM Method D3556-79 for the deposition on glassware during mechanical dishwashing is used to evaluate the buildup of spots and film on glassware. 50 grams of Cascade and 50 grams of regular powder detergent and 28 grams of concentrated powder detergent is used in each test. All testing reported is done in Kenmore Model 587.1548580 and/or model 587.1546580 Automatic Dishwasher. The water wash temperature is 120° F and the water has 300 ppm hardness and the below results are the average of four washes using 6 to 10 glass tumblers per wash.

The results obtained are reported below.

EP 0 395 186 A2

	Spot	Film
Cascade Powder	1	2
Regular Powder	1	1.8
Concentrated Powder	1	2.8

The Cascade powder gives less film than the concentrated dual bleach ADD compositions. There is no difference in the spot scores.

Spot/Film Scale

Spot on Glasses

- 1 = no spots
- 2 = 1-2 spots
- 3 = 25 percent of glass covered with spots
- 4 = 50 percent of glass covered with spots
- 5 = 100 percent of glass covered with spots

Film on Glasses

- 1 = best - no film
- 2 = film slightly apparent
- 3 = increase in noticeable film
- 4 = filming significant
- 5 = filming becoming excessive
- 6 = filming highly excessive

Example 2

Following the teachings of the invention a regular automatic dishwasher powder detergent composition is formulated using the below named ingredients in the amounts indicated.

	Weight Percent
Sodium Tripolyphosphate ⁽¹⁾	31-34
Sodium Carbonate	19
Sodium Sulfate	19
Nonionic Surfactant ⁽²⁾	3.0
Sodium Silicate	12.0
Sodium Bromide ⁽³⁾	0-3
Sodium Dichloroisocyanurate (Available chlorine 1%)	1.8
Perfume	—
Moisture	—

(1) STPP concentration varied with bromide.

(2) Tergitol MDS-42.

(3) Sodium bromide concentration is varied from 0 (control) to 3.0 wt.% for comparison purposes. There are five formulations prepared containing 0 (control), 0.5, 1.0, 1.5 and 3.0 wt.% sodium bromide.

The formulations and soiled dishware are prepared following the procedure of Example 1 except that porridge is substituted for the oatmeal. The multi-soil cleaning test is carried out following the procedure of

EP 0 395 186 A2

Example 1, but using GE Model GSD 1200G Automatic Dishwasher at 120° F wash temperature and tap water with about 110 ppm water hardness.

The test results that are obtained are reported in the below table.

Test	ADD Formulation Sodium Bromide Concentration Weight %	Percent Porridge Removal	Percent Egg Removal	Mole Ratio Bromide To Available Chlorine
A	0	<20	72	-
B	0.3	100	69	0.10
C	0.5	98	46	0.17
D	1.0	100	34	0.34
E	1.5	100	25	0.51
F	3.0	100	10	1.03

The above information illustrates the effect on the removal of proteineous soil and starch carbohydrate soil by varying the mole ratio of bromide to available chlorine in the formulation.

Example 3

In accordance with the present invention a regular automatic dishwasher powder detergent composition is formulated using the below named ingredients in the amounts indicated.

Component	Weight Percent
Sodium Tripolyphosphate	36
Sodium Carbonate	18
Sodium Sulfate	18
Nonionic Surfactant	3.0
Sodium Silicate (1:2.4)	12.0
Sodium Bromide	0.30
Sodium Dichloroisocyanurate (ACI 56) ⁽¹⁾	2.5
Color, Perfume	—
Moisture	—

(1) 1.4% available chlorine.

The mole ratio of bromide to available chlorine is 0.07.

About 50 grams of the above formulation is tested in an automatic dishwasher machine to clean dishes containing baked on proteinaceous egg soil and baked on starchy carbohydrate pasta soil.

The dishes after a normal wash cycle are removed from the dishwasher and are found to be substantially reduced in both the proteinaceous egg soil and the starchy carbohydrate pasta soil.

Example 4

Following the teachings of the invention a concentrated automatic dishwasher powder detergent composition is formulated using the below named ingredients.

Ingredient	Weight Percent
Sodium Citrate	60.0
Sodium Carbonate	-
Sodium Sulfate	-
Nonionic Surfactant	4.0
Sodium Silicate (1:2.4)	22.0
Sodium Bromide	0.60
Sodium Dichloroisocyanurate (ACI 56) ⁽¹⁾	5.0
Color, Perfume	—
Moisture	—

(1) 2.8% available chlorine.

The mole ratio of bromide to available chlorine is 0.07.

About 28 grams of the above concentrated formulation is tested in an automatic dishwasher machine to clean dishes containing baked on proteinaceous egg soil and baked on starchy carbohydrate pasta soil.

The dishes after a normal wash cycle are removed from the dishwasher and are found to be substantially reduced in both the proteinaceous egg soil and the starchy carbohydrate pasta soil.

The dual bleach automatic dishwashing powder detergent compositions of the present invention provided improved removal of proteinaceous soils and starchy carbohydrate soils.

The invention is not to be limited by the above disclosure and examples which are given as illustrations only. The invention is to be interpreted in accordance with the below claims.

Claims

1. An automatic dishwashing detergent composition having improved cleaning performance against both proteinaceous and carbohydrate soils comprising at least one ingredient selected from the group consisting of organic detergent, detergent builder, foam inhibitors and mixtures thereof, and a dual bleach system comprising a hypochlorite source and a bromide compound wherein the mole ratio of bromide to available chlorine is 0.04 to 0.12.

2. The compositions of claim 1 wherein the hypochlorite source contains 0.5 to 5 wt.% available chlorine and the bromide compound is in an amount of 0.1 to 3.0%.

3. An automatic dishwasher composition comprising approximately by weight:

(a) 20 to 70% organic or inorganic detergent builder;

(b) 2.5 to 40% sodium silicate;

(c) 0 to 30% alkali metal carbonate;

(d) 0.1 to 6% chlorine bleach stable, water-dispersible organic detergent active material;

(e) 0 to 6% chlorine bleach stable foam depressant;

(f) chlorine bleach compound capable of forming hypochlorite on addition to water in an amount to provide about 0.5 to 5% of available chlorine;

(g) a sufficient amount of bromide compound to provide a mole ratio of bromide to available chlorine of 0.05 to 0.095; and

(h) 0 to 8% of sodium silicate.

4. The composition of claim 3 wherein the chlorine bleach compound is a member selected from the group of chlorocyanurates, chloroisocyanurates, alkali and alkaline earth hypochlorites.

5. The composition of claim 3 wherein the bromide compound is a member selected from the of alkali and alkaline earth metal bromides.

6. An automatic dishwasher powder detergent composition comprising approximately by weight:

(a) 10 to 40% alkali metal tripolyphosphate;

(b) 10 to 35% sodium silicate;

(c) 5 to 25% alkali metal carbonate;

(d) 0.1 to 5% chlorine bleach stable, water dispersible organic nonionic detergent active material;

(e) 0 to 5% chlorine bleach stable foam depressant;

(f) chlorine bleach compound selected from the group of chlorocyanurates, chloroisocyanurates, alkali

and alkaline earth metal hypochlorites in an amount to provide about 1 to 3% of available chlorine;

(g) a sufficient amount of bromide compound to provide a mole ratio of bromide compound to available chlorine of 0.05 to 0.095;

(h) 0 to 8% of sodium silicate; and

5 (i) 0 to 8% moisture.

7. The composition of claim 6 wherein the chlorine compound is sodium dichloroisocyanurate or sodium trichloroisocyanurate or mixtures thereof.

8. The composition of claim 6 wherein the bromide compound is an alkali metal or alkaline earth metal bromide.

10 9. The composition of claim 6 wherein the bromide compound is sodium bromide.

10. The composition of claim 6 wherein the chlorine compound is calcium hypochlorite.

11. The composition of claim 6 wherein the chlorine compound is in an amount of 1 to 10 wt.%.
12. The composition of claim 6 wherein the bromide compound is in an amount of 0.10 to 3 wt.%.

13. A method for cleaning soiled dishware which contain both proteinaceous soils and carbohydrate
15 soils which comprises contacting the soiled dishware in an automatic dishwashing machine in an aqueous washbath having dispersed therein an effective amount of the composition of claim 1 to obtain clean dishware reduced in proteinaceous soils and carbohydrate soils.

14. A method for cleaning soiled dishware which contain both proteinaceous soils and carbohydrate
20 soils which comprises contacting the soiled dishware in an automatic dishwashing machine in an aqueous washbath having dispersed therein an effective amount of the composition of claim 6 to obtain clean dishware of reduced in proteinaceous soils and carbohydrate soils.

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