

# (11) EP 4 227 391 A1

(12)

## **EUROPEAN PATENT APPLICATION**

(43) Date of publication: 16.08.2023 Bulletin 2023/33

(21) Application number: 23176658.5

(22) Date of filing: 02.03.2015

(51) International Patent Classification (IPC):

C11D 1/66 (2006.01) C11D 3/37 (2006.01) C11D 1/00 (2006.01) C11D 1/72 (2006.01)

(52) Cooperative Patent Classification (CPC): C11D 3/10; C11D 1/825; C11D 3/3757; C11D 11/0035; C11D 17/0052; C11D 17/0091; C11D 1/008; C11D 1/72

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **07.03.2014 US 201461949377 P 07.03.2014 US 201461949387 P** 

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC: 15759090.2 / 3 114 197

(71) Applicant: Ecolab USA Inc. St. Paul, MN 55102 (US)

(72) Inventors:

 ROERDINK-LANDER, Monique Minnesota, 55121 (US)  SILVERNAIL, Carter M. St. Paul, 55102 (US)

 DAHLQUIST HOWLETT, Erin Jane Minnesota, 55121 (US)

 WALTERS, Kerrie Minnesota, 55121 (US)

(74) Representative: Godemeyer Blum Lenze
Patentanwälte
Partnerschaft mbB - werkpatent
An den Gärten 7
51491 Overath (DE)

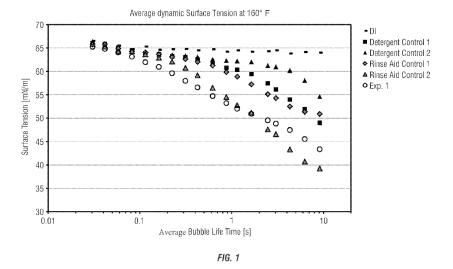
#### Remarks:

This application was filed on 01-06-2023 as a divisional application to the application mentioned under INID code 62.

## (54) DETERGENT COMPOSITION THAT PERFORMS BOTH A CLEANING AND RINSING FUNCTION

(57) Industrial 2-in-1 cleaning compositions providing both detergency and rinseability in a single cleaning composition are disclosed. Alkali metal carbonate-based cleaning compositions and methods of both making and using the same provide user-friendly, solid, detergent

compositions without the need for using a separate rinse aid composition. The compositions and methods are particularly well suited for use in industrial cleaning using alkali metal carbonate compositions that beneficially provide cleaning and rinseability in the rinse cycle.



## Description

15

30

35

40

50

#### **FIELD OF THE INVENTION**

**[0001]** The invention relates to an industrial 2-in-1 cleaning composition providing both detergency and rinse aid efficacy in a single cleaning composition. In particular, compositions and methods of both making and using the same provide a user-friendly, solid, detergent composition without the need for using a separate rinse aid composition. The compositions and methods are particularly well suited for use in industrial cleaning using alkali metal carbonate compositions that beneficially provide cleaning and rinseability to permit the use of a potable water rinse without the addition of a separate rinse agent.

#### **BACKGROUND OF THE INVENTION**

[0002] Alkaline detergents are used extensively to clean articles in both consumer and industrial dish machines. Alkaline detergents are extensively used because of their ability to remove and emulsify fatty, oily, hydrophobic soils. However, alkaline detergents have the disadvantage of requiring a rinse aid to prevent the formation of films on glass and other substrate surfaces contacted by the alkaline detergent. Filming is caused in part by using alkaline detergents in combination with certain water types (including hard water), and water temperatures. A solution to the generation of hard water films has been to employ rinse aids to remove such films. However, the need for rinse aids increases the cost associated with alkaline detergents for both the formulation of the cleaning compositions as well as the additional costs associated with heated water for rinsing steps.

**[0003]** Additionally, rinse aids are used in a rinse cycle following the wash cycle to enhance drying time, as well as reduce any cleaning imperfections (including the removal of films). Additional benefits and methods of using rinse aids are described in U.S. Patent No. RE 38262, which is herein incorporated by reference in its entirety. The addition of rinse aids to a ware wash rinse cycle requires use of GRAS (generally recognized as safe) ingredients as well as wall space for the installation of both a detergent dispenser and a rinse aid dispenser.

**[0004]** There is a need for alternative, effective cleaning compositions that provide the desired cleaning results and at the same time reduce the number of components required for cleaning and rinsing.

**[0005]** Accordingly, it is an objective of the claimed invention to develop an alkaline detergent composition that provides good cleaning performance and good rinseability in a potable water rinse without the use of an added rinse aid in the rinse cycle.

**[0006]** A further object of the invention is to provide a carbonate-based alkaline detergent employing a combination of surfactants, and optionally polymers, to provide good cleaning performance and rinseability without the use of a rinse aid in the cleaning composition.

**[0007]** A further object of the invention is to provide a carbonate-based alkaline detergent employing a combination of surfactants, and optionally polymers, providing at least substantially similar cleaning and rinsing efficacy as a conventional two part detergents and rinse aids.

[0008] Other objects, advantages and features of the present invention will become apparent from the following specification taken in conjunction with the accompanying drawings.

### **BRIEF SUMMARY OF THE INVENTION**

**[0009]** An advantage of the invention is industrial detergent compositions providing both detergency and rinseability in a single cleaning composition, thus eliminating the need for an additional rinse aid composition. The composition of the invention provides thus a user-friendly, solid, 2-in-1 cleaning and rinsing action, beneficially eliminating a distinct rinse aid from the industrial warewashing compositions and methods of use. The alkaline detergent compositions according to the invention beneficially provide both good cleaning performance and rinseability in a potable water rinse without the use of an added rinse aid in the rinse cycle.

**[0010]** In an embodiment, the present invention provides a composition comprising a carbonate alkalinity source in combination with nonionic surfactants, where the composition replaces the separate use of both a dish machine detergent and a rinse additive due to the superior cleaning and rinseability of the composition. The detergent compositions can also include polymers, such as a polycarboxylic acid polymer, builders, water conditioning agents, neutralizing agents, sanitizers, etc.

[0011] In another embodiment, the present invention provides methods of cleaning articles in an industrial dish machine using a carbonate-based alkaline detergent comprising an alkali metal carbonate and nonionic surfactants. The invention also pertains to a method of cleaning articles in an industrial dish machine using the steps of supplying the alkaline 2-in-1 composition, inserting the composition into a dispenser in a dish machine, forming a wash solution with the composition and water, contacting soil on an article in the dish machine with the wash solution, removing the soil, and rinsing

the article using the same alkaline 2-in-1 cleaning composition and no additional rinse aids.

**[0012]** While multiple embodiments are disclosed, still other embodiments of the present invention will become apparent to those skilled in the art from the following detailed description, which shows and describes illustrative embodiments of the invention. Accordingly, the drawings and detailed description are to be regarded as illustrative in nature and not restrictive.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

### [0013]

5

10

15

20

25

30

35

40

45

50

FIG. 1 shows a graph of the average dynamic surface tension of an experimental formulation (Exp. 1) in comparison to phosphate-based alkaline detergents as well as nonionic-based rinse aids at a temperature of 160°F as a function of the average bubble life time at use concentrations. The values shown are averages of three independent measurements. According to an embodiment of the invention, the experimental formulation demonstrates a quick decrease and significant drop in surface tension, similar to a well-performing commercial rinse aid, such as rinse aid control 2. FIG. 2 shows a graph of the average dynamic surface tension of an experimental formulation (Exp. 2) in comparison to phosphate-based alkaline detergents as well as nonionic-based rinse aids at a temperature of 160°F as a function of the average bubble life time at use concentrations. The values shown are averages of three independent measurements. According to an embodiment of the invention, the experimental formulation demonstrates a quick decrease and significant drop in surface tension, similar to a well-performing commercial rinse aid, such as rinse aid control 2.

**[0014]** Various embodiments of the present invention will be described in detail with reference to the drawings, wherein like reference numerals represent like parts throughout the several views. Reference to various embodiments does not limit the scope of the invention. Figures represented herein are not limitations to the various embodiments according to the invention and are presented for exemplary illustration of the invention.

[0015] The invention relats to the following aspects:

- 1. An alkaline detergent and rinsing composition comprising:
  - an alkalinity source comprising an alkali metal carbonate; and
  - at least two nonionic surfactants, wherein said nonionic surfactants comprises an alcohol alkoxylate and an alkyl alkoxylate; and
  - a builder;
  - wherein said composition performs both a cleaning and rinsing function.
- 2. The composition of aspect 1, wherein said alkalinity source is present from about 10 wt-% to about 90 wt-%, wherein said nonionic surfactants are present from about 0.1 to about 80 wt-%.
- 3. The composition of aspect 1, wherein said alcohol alkoxylate and alkyl alkoxylate are in a ratio of between about 3:1 to 1:3.
- 4. The composition of aspect 1, wherein said composition provides substantially similar cleaning and rinsing performance as separate detergent and rinse aid compositions.
- 5. The composition of aspect 1, further comprising a neutralizing agent in an amount between 0.1 wt-% and about 50 wt-%.
  - 6. The composition of aspect 5, wherein the alkalinity source comprises an alkali metal carbonate, wherein the alkalinity source is substantially free of alkali metal hydroxide, and wherein the neutralizing agent comprises up to about 10 wt-% alkali metal hydroxide.
  - 7. The composition of aspect 1, further comprising an enzyme.
  - 8. The composition of aspect 7, wherein the enzyme is a protease, lipase and/or amylase.
  - 9. The composition of aspect 1, wherein the alkyl alkoxylate is present from about 0.1 wt-% to about 15 wt-%.
  - 10. An alkaline detergent and rinsing composition comprising:

an alkalinity source comprising an alkali metal carbonate;

at least two nonionic surfactants, wherein said nonionic surfactants comprise an alcohol alkoxylate and a EO/PO copolymer;

a builder; and

5

10

20

25

30

35

40

50

55

- a polymer comprising a polycarboxylic acid polymer, copolymer, and/or terpolymer; wherein said composition performs both a cleaning and rinsing function.
- 11. The composition of aspect 10, wherein said alkalinity source is present from about 10 wt-% to about 90 wt-%, wherein said nonionic surfactant is present from about 0.1 to about 80 wt-%, and wherein said polymer is present from about 0.1 to about 50 wt-%.
- 12. The composition of aspect 10, wherein said EO/PO copolymer and alcohol alkoxylate are in a ratio of between about 3:1 to 1:3.
- 13. The composition of aspect 10, wherein said composition provides substantially similar cleaning and rinsing performance as separate detergent and rinse aid compositions.
  - 14. The composition of aspect 10, further comprising a neutralizing agent in an amount between 0.1 wt-% and about 50 wt-%.
  - 15. The composition of aspect 10, wherein the polymer is present from about 0.1 wt-% to about 40 wt-% and comprises a polyacrylic acid polymer, copolymer, and/or terpolymer.
  - 16. The composition of aspect 15, wherein the polyacrylic acid polymer, copolymer, and/or terpolymers is an acrylic/maleic acid copolymer.
    - 17. The composition of aspect 14, wherein the alkalinity source comprises an alkali metal carbonate, wherein the alkalinity source is substantially free of alkali metal hydroxide, and wherein the neutralizing agent comprises up to about 10 wt-% alkali metal hydroxide.
    - 18. The composition of aspect 17 further comprising an enzyme.
    - 19. A method of cleaning and rinsing ware comprising: contacting ware with an alkaline detergent composition of aspect 1 or 10.
    - 20. The method of aspect 19, wherein said alkalinity source is present from about 10 wt-% to about 90 wt-%, and wherein said nonionic surfactants are present from about 0. 1 to about 80 wt-%.
  - 21. The method of aspect 19, wherein said alcohol alkoxylate and alkyl alkoxylate are in a ratio of between about 3:1 to 1:3
    - 22. The method of aspect 19, wherein the alkaline detergent composition further comprises a neutralizing agent in an amount between about 0.1 wt-% and about 50 wt-%.
- 23. The method of aspect 22, wherein the alkalinity source comprises an alkali metal carbonate, wherein the alkalinity source is substantially free of alkali metal hydroxide, and wherein the neutralizing agent comprises up to about 10 wt-% alkali metal hydroxide.
  - 24. The method of aspect 19, wherein the alkaline determine composition further comprises a protease, lipase and/or amylase enzyme.
    - 25. The method of aspect 19, wherein the alkyl alkoxylate is present from about 0.1 wt-% to about 15 wt-%.
  - 26. The composition of aspects 1 or 10, wherein the alkaline detergent is a cast, extruded, or pressed solid.

## **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

[0016] The present invention relates to a 2-in-1 industrial alkaline cleaning compositions which provide suitable cleaning

and rinseability while employing a carbonate-based alkaline detergent and a combination of surfactants. In an exemplary embodiment, the nonionic surfactants create an efficacious aqueous rinse with potable water. The embodiments of this invention are not limited to particular alkaline detergents, which can vary and are understood by skilled artisans based upon the disclosure provided herein. It is further to be understood that all terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting in any manner or scope. For example, as used in this specification and the appended claims, the singular forms "a," "an" and "the" can include plural referents unless the content clearly indicates otherwise. Further, all units, prefixes, and symbols may be denoted in its SI accepted form. [0017] Numeric ranges recited within the specification are inclusive of the numbers defining the range and include each integer within the defined range. Throughout this disclosure, various aspects of this invention are presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range. [0018] So that the present invention may be more readily understood, certain terms are first defined. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which embodiments of the invention pertain. Many methods and materials similar, modified, or equivalent to those described herein can be used in the practice of the embodiments of the present invention without undue experimentation, the preferred materials and methods are described herein. In describing and claiming the embodiments of the present invention, the following terminology will be used in accordance with the definitions set out below. [0019] The term "about," as used herein, refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients used to make the compositions or carry out the methods; and the like. The term "about" also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

10

30

35

40

50

55

**[0020]** The term "actives" or "percent actives" or "percent by weight actives" or "actives concentration" are used interchangeably herein and refers to the concentration of those ingredients involved in cleaning expressed as a percentage minus inert ingredients such as water or salts.

[0021] As used herein, the term "alkyl" refers to a straight or branched chain monovalent hydrocarbon group optionally containing one or more heteroatomic substitutions independently selected from S, O, Si, or N. Alkyl groups generally include those with one to twenty atoms. Alkyl groups may be unsubstituted or substituted with those substituents that do not interfere with the specified function of the composition. Substituents include alkoxy, hydroxy, mercapto, amino, alkyl substituted amino, or halo, for example. Examples of "alkyl" as used herein include, but are not limited to, methyl, ethyl, n-propyl, n-butyl, n-pentyl, isobutyl, isopropyl, and C8-C20 alkyl chains and the like. In addition, "alkyl" may include "alkylenes", "alkenylenes", or "alkylynes".

**[0022]** As used herein, the term "alkylene" refers to a straight or branched chain divalent hydrocarbon group optionally containing one or more heteroatomic substitutions independently selected from S, O, Si, or N. Alkylene groups generally include those with one to twenty atoms. Alkylene groups may be unsubstituted or substituted with those substituents that do not interfere with the specified function of the composition. Substituents include alkoxy, hydroxy, mercapto, amino, alkyl substituted amino, or halo, for example. Examples of "alkylene" as used herein include, but are not limited to, methylene, ethylene, propane-1,3-diyl, propane-1,2-diyl and the like.

[0023] As used herein, the term "alkenylene" refers to a straight or branched chain divalent hydrocarbon group having one or more carbon-carbon double bonds and optionally containing one or more heteroatomic substitutions independently selected from S, O, Si, or N. Alkenylene groups generally include those with one to twenty atoms. Alkenylene groups may be unsubstituted or substituted with those substituents that do not interfere with the specified function of the composition. Substituents include alkoxy, hydroxy, mercapto, amino, alkyl substituted amino, or halo, for example. As used herein, the term "alkylyne" refers to a straight or branched chain divalent hydrocarbon group having one or more carbon-carbon triple bonds and optionally containing one or more heteroatomic substitutions independently selected from S, O, Si, or N. Alkylyne groups generally include those with one to twenty atoms. Alkylyne groups may be unsubstituted or substituted with those substituents that do not interfere with the specified function of the composition. Substituents include alkoxy, hydroxy, mercapto, amino, alkyl substituted amino, or halo, for example.

**[0024]** As used herein, the term "alkoxy", refers to --O--alkyl groups wherein alkyl is as defined above. As used herein, the term "cleaning" refers to a method used to facilitate or aid in soil removal, bleaching, microbial population reduction, and any combination thereof.

**[0025]** The term "generally recognized as safe" or "GRAS," as used herein refers to components classified by the Food and Drug Administration as safe for direct human food consumption or as an ingredient based upon current good

manufacturing practice conditions of use, as defined for example in 21 C.F.R. Chapter 1, §170.38 and/or 570.38.

**[0026]** As used herein, the term "soil" or "stain" refers to a polar or non-polar substances which may or may not contain particulate matter such as, but not limited to mineral clays, sand, natural mineral matter, carbon black, graphite, kaolin, environmental dust and food soils such as polyphenols starches, proteins, oils and fats, etc.

**[0027]** As used herein, the term "substantially free" refers to compositions completely lacking the component or having such a small amount of the component that the component does not affect the performance of the composition. The component may be present as an impurity or as a contaminant and shall be less than 0.5 wt-%. In another embodiment, the amount of the component is less than 0.1 wt-% and in yet another embodiment, the amount of component is less than 0.01 wt-%.

[0028] The term "substantially similar cleaning performance" refers generally to achievement by a substitute cleaning product or substitute cleaning system of generally the same degree (or at least not a significantly lesser degree) of cleanliness or with generally the same expenditure (or at least not a significantly lesser expenditure) of effort, or both.

[0029] The term "threshold agent" refers to a compound that inhibits crystallization of water hardness ions from solution, but that need not form a specific complex with the water hardness ion. Threshold agents include but are not limited to a polyacrylate, a polymethacrylate, an olefin/maleic copolymer, and the like.

**[0030]** As used herein, the term "ware" refers to items such as eating and cooking utensils, and dishes. As used herein, the term "warewashing" refers to washing, cleaning, or rinsing ware. Ware also refers to items made of plastic. Types of plastics that can be cleaned with the compositions according to the invention include but are not limited to, those that include polycarbonate polymers (PC), acrilonitrile-butadiene-styrene polymers (ABS), and polysulfone polymers (PS). Other exemplary plastics that can be cleaned using the compounds and compositions of the invention include polyethylene terephthalate (PET) and plastics from melamine resin.

**[0031]** The term "weight percent," "wt-%," "percent by weight," "% by weight," and variations thereof, as used herein, refer to the concentration of a substance as the weight of that substance divided by the total weight of the composition and multiplied by 100. It is understood that, as used here, "percent," "%," and the like are intended to be synonymous with "weight percent," "wt-%," etc.

**[0032]** The methods and compositions of the present invention may comprise, consist essentially of, or consist of the components and ingredients of the present invention as well as other ingredients described herein. As used herein, "consisting essentially of" means that the methods and compositions may include additional steps, components or ingredients, but only if the additional steps, components or ingredients do not materially alter the basic and novel characteristics of the claimed methods and compositions.

Alkaline 2-in-1 Detergent Compositions

Alkalinity Source

10

20

30

35

40

45

50

55

[0033] The alkaline detergent compositions include an alkalinity source. The alkalinity source comprises an alkali metal carbonate. Examples of suitable alkalinity sources include but are not limited to: alkali metal carbonates, such as sodium carbonate, potassium carbonate, bicarbonate, sesquicarbonate, and mixtures thereof. In an aspect, the alkaline detergent compositions do not include a hydroxide alkalinity source. The alkalinity source controls the pH of the use solution when water is added to the detergent composition to form a use solution. The pH of the use solution must be maintained in the alkaline range in order to provide sufficient detergency properties. In one embodiment, the pH of the use solution is between about 9 and about 12. Particularly, the pH of the use solution is between about 9.5 and about 11.5. [0034] In certain embodiments, the alkalinity source may also function as a hydratable salt to form a solid composition. The hydratable salt can be referred to as substantially anhydrous. By substantially anhydrous, it is meant that the component contains less than about 2% by weight water based upon the weight of the hydratable component. The amount of water can be less than about 1% by weight, and can be less than about 0.5% by weight. As one skilled in the art will ascertain, there is no requirement that the hydratable salt be completely anhydrous. In certain embodiments, there is also water of hydration to hydrate the alkalinity source (i.e. hydratable salt). It should be understood that the reference to water includes both water of hydration and free water. The phrase "water of hydration" refers to water which is somehow attractively bound to a non-water molecule. An exemplary form of attraction includes hydrogen bonding. The water of hydration also functions to increase the viscosity of the mixture during processing and cooling to prevent separation of the components. The amount of water of hydration in the detergent composition will depend on the alkalinity source/hydratable salt. In addition to water of hydration, the detergent composition may also have free water which isn't attractively bound to a non-water molecule.

[0035] In an aspect, the alkaline detergent compositions include from about 10 wt-% - 95 wt-% alkalinity source, from about 25 wt-% - 90 wt-% alkalinity source, from about 40 wt-% - 85 wt-% alkalinity source, preferably from about 45 wt-% - 75 wt-% alkalinity source. In addition, without being limited according to the invention, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

#### Surfactants

10

15

20

30

40

45

[0036] The 2-in-1 alkaline compositions according to the invention employ a combination of surfactants to provide good cleanability and rinseability. In an embodiment, the surfactants of the alkaline detergent compositions include at least two nonionic surfactants. In embodiment, the nonionic surfactants comprise an alcohol alkoxylate and an alkyl alkoxylate. In a still further embodiment, the nonionic surfactants are selected from the group consisting of an alcohol alkoxylate, an alkyl alkoxylate, an EO/PO copolymer, and combinations thereof. In an aspect, the alkaline detergent compositions include from about 0.1 wt-% - 30 wt-% surfactants, from about 0.1 wt-% - 25 wt-% surfactants, from about 0.1 wt-% - 20 wt-% surfactants, from about 1 wt-% - 15 wt-% surfactants, from about 1 wt-% - 10 wt-% surfactants, and preferably from about 5 wt-% - 10 wt-% surfactants. In addition, without being limited according to the invention, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

[0037] In some embodiments, the ratio of the alcohol alkoxylate to the alkyl alkoxylate is from about 1:5 to about 5:1, from about 1:3 to about 3:1, from about 1:2 to about 2:1, and preferably about 1:1. In an exemplary embodiment, the nonionic surfactants include an alkyl alkoxylate and alcohol alkoxylate in a ratio of about 1:1, from about 1:5 to about 5:1, from about 1:3 to about 3:1, or from about 1:2 to about 2:1. In a preferred aspect, the alkaline detergent composition includes an alkyl alkoxylate and alcohol alkoxylate in a ratio of about 1:1.

#### Alcohol Alkoxylates

[0038] The 2-in-1 alkaline compositions according to the invention employ at least two nonionic surfactant comprising an alcohol alkoxylate. Suitable alcohol alkoxylates include ethylene oxide, propylene oxide, and butylene oxide groups and mixtures thereof. Particularly, suitable alcohol alkoxylates can have between about 1 and about 30 moles of alkyl oxide and carbon chains between about 4 and about 20 carbons in length. In a preferred embodiment the alcohol ethoxylate may be a C8-C18 alcohol alkoxylate with about 10 to about 40 moles of alkyl oxide. In a more preferred embodiment the alcohol alkoxylate may be a C8-C16 alcohol alkoxylate with about 10 to about 30 moles of alkyl oxide. In an even more preferred embodiment, the alcohol alkoxylate may be a C10-C12 alcohol alkoxylate with about 15 to about 25 moles of alkyl oxide. Examples of preferred alcohol alkoxylates are available under the brands Surfonic (available from Huntsman), Rhodasurf (available from Rhodia), Novel (available from Sasol), Lutensol (available from BASF).

[0039] In an aspect of the invention, the alkaline detergent compositions include from about 0.1 wt-% to about 15wt-% alcohol alkoxylate, from about 0.1 wt-% to about 10 wt-% alcohol alkoxylate, from about 0.1 wt-% to about 7 wt-%, or from about 1 wt-% to about 49 wt-%.

### Alkyl Alkoxylates

[0040] The 2-in-1 alkaline compositions according to the invention employ an alkyl alkoxylate. Alkyl alkoxylates having ethylene oxide and/or propylene oxide derivatives are particularly suitable for the alkaline compositions. In other embodiments, the alkyl alkoxylate includes an ethylene oxide, a propylene oxide, a butylene oxide, a pentalene oxide, a hexylene oxide, a heptalene oxide, an octalene oxide, a nonalene oxide, a decylene oxide, and mixtures thereof. The alkyl group can be C8-C18, linear or branched.

**[0041]** In an embodiment of the invention the alkyl alkoxylate can be an EO/PO copolymer. The EO/PO copolymer may have from about 1 to about 50 moles of EO and from about 1 to about 50 moles of PO. In a preferred embodiment, the EO/PO copolymer is a block polymer. In another aspect of the invention, the EO/PO copolymer does not contain a C8-18 alkyl group, or even any alkyl groups.

[0042] These EO/PO copolymer surfactants can include a compact alcohol EO/PO surfactant where the EO and PO groups are in small block form, or random form. In other embodiments, the alkyl alkoxylate includes an ethylene oxide, a propylene oxide, a butylene oxide, a pentalene oxide, a hexylene oxide, a heptalene oxide, an octalene oxide, a nonalene oxide, a decylene oxide, and mixtures thereof. The alkyl group can be C10-C18, linear or branched. In an aspect, the EO/PO copolymer surfactants are particularly suitable for use in the 2-in-1 alkaline compositions in combination with an alcohol alkoxylate surfactant. Exemplary commercially available surfactants are available, for example, under the tradename Pluronic® and Pluronic R, (commercially available from BASF), Tetronic (available from Dow) and Surfonic (available from Huntsman).

**[0043]** Some examples of ethylene oxide and/or propylene oxide derivative surfactants that may be used include polyoxyethylene-polyoxypropylene block copolymers, or the like, or derivatives thereof. Some examples of polyoxyethylene-polyoxypropylene block copolymers include those having the following formulae:

(EO)x(PO)y(EO)x

(PO)y(EO)x(PO)y

55

$$(PO)_{V}(EO)_{X}(PO)_{V}(EO)_{X}(PO)_{V}$$

wherein EO represents an ethylene oxide group, PO represents a propylene oxide group, and x and y reflect the average molecular proportion of each alkylene oxide monomer in the overall block copolymer composition. In an aspect of the invention, a preferred EO/PO copolymer is represented by the formula (EO)x(PO)y(EO)x. In a further aspect of the invention, a preferred EO/PO copolymer is represented by the formula (PO)y(EO)x(PO)y. In some embodiments, x is in the range of about 5 to about 50, y is in the range of about 1 to about 50, and x plus y is in the range of about 6 to about 200. It should be understood that each x and y in a molecule can be different. In some embodiments, the material can have a molecular weight greater than about 200 and less than about 25,000. For example, in some embodiments, the material can have a molecular weight in the range of about 500 to about 25,000, or in the range of about 1000 to about 20,000.

[0044] In some embodiments, the EO/PO surfactants may have between about 1 and about 50 ethylene oxide groups and from about 1 to about 50 propylene oxide groups. In some embodiments, the material can have a molecular weight greater than about 400, and in some embodiments, greater than about 500. For example, in some embodiments, the material can have a molecular weight (g/mol) in the range of about 500 to about 7000 or more, or in the range of about 950 to about 4000 or more, or in the range of about 1000 to about 3100 or more, or in the range of about 2100 to about 6700 or more, or in the range of about 2500 to about 4200 or more.

**[0045]** The treatise Nonionic Surfactants, edited by Schick, M. J., Vol. 1 of the Surfactant Science Series, Marcel Dekker, Inc., New York, 1983 provides further description of nonionic compounds generally employed in the practice of the present invention. A typical listing of nonionic classes, and species of these surfactants, is given in U.S. Pat. No. 3,929,678 issued to Laughlin and Heuring on Dec. 30, 1975. Further examples are given in "Surface Active Agents and detergents" (Vol. I and II by Schwartz, Perry and Berch). Each of these references is herein incorporated by reference in their entirety.

**[0046]** In an aspect of the invention, the alkaline detergent compositions include from about 0.1 wt-% to about 15 wt-% of the alkyl alkoxylate, from about 0.1 wt-% to about 10 wt-% of the alkyl alkoxylate), or from about 0.1 wt-% to about 7 wt-% the alkyl alkoxylate.

#### Polymer

5

10

20

30

35

40

45

50

**[0047]** The present invention can include a polymer comprised of at least one polycarboxylic acid polymer, copolymer, and/or terpolymer. Particularly suitable polycarboxylic acid polymers of the present invention, include, but are not limited to, polyacrylic acid polymers and copolymers, polymaleic polymers and copolymers, and acrylic/maleic copolymers. Other suitable polycarboxylic acid polymers include polymaleic acid homopolymers, polyacrylic acid copolymers, and maleic anhydride/olefin copolymers. In a preferred embodiment, the polymer comprises, consists essentially of, or consists of a polyacrylic acid polymer, copolymer, terpolymer and/or salts thereof.

**[0048]** The detergent compositions of the present invention can use polyacrylic acid polymers, copolymers, and/or terpolymers. Polyacrylic acids have the following structural formula:

where n is any integer. Examples of suitable polyacrylic acid polymers, copolymers, and/or terpolymers, include but are not limited to, the polymers, copolymers, and/or terpolymers of polyacrylic acids,  $(C_3H_4O_2)_n$  or 2-Propenoic acid, acrylic acid, polyacrylic acid, propenoic acid.

**[0049]** In an embodiment of the present invention, particularly suitable acrylic acid polymers, copolymers, and/or terpolymers have a molecular weight between about 100 and about 10,000, in a preferred embodiment between about 500 and about 7,000, in an even more preferred embodiment between about 1,000 and about 5,000, and in a most preferred embodiment between about 1,500 and about 4,500.

[0050] Polymaleic acid  $(C_4H_2O_3)x$  or hydrolyzed polymaleic anhydride or cis-2-butenedioic acid homopolymer, has the structural formula:

where n and m are any integer. Examples of polymaleic acid homopolymers, copolymers, and/or terpolymers (and salts thereof) which may be used for the invention are particularly preferred are those with a molecular weight of about 100 and about 10,000, more preferably between about 500 and about 7,000, in an even more preferred embodiment between about 1,000 and about 5,000, and in a most preferred embodiment between about 1,500 and about 4,500. Commercially available polymaleic acid homopolymers include the Belclene 200 series of maleic acid homopolymers from BWA™ Water Additives, 979 Lakeside Parkway, Suite 925 Tucker, GA 30084, USA and Aquatreat AR-801 available from AkzoNobel

[0051] In a preferred embodiment, the polymer is a copolymer of acrylic acid and maleic acid. Preferably, an acrylic/maleic acid copolymer an acrylic/maleic copolymer has a molecular weight from about 1,000 to about 10,000 g/mol, preferably a molecular weight between about 1,000 to about 5,000 g/mol. An example of a suitable acrylic/maleic acid copolymer includes, but is not limited to, Acusol 448 from The Dow Chemical Company, Wilmington Delaware, USA.

[0052] In embodiments employing a polymer, it is expected that the compositions will include the polymer in an amount between about 0.1 wt-% and about 50 wt-%, between about 0.1 wt-% and about 40 wt-%, between about 0.1 wt-% and about 30 wt-%, or 1 wt-% and about 20 wt-%. All ranges recited are inclusive of the numbers contained therein. The polymer of the present invention can comprise, consist essentially of, or consist of at least one polyacrylic acid polymer, copolymer, and/or terpolymer. In addition, without being limited according to the invention, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

### Additional Functional Ingredients

5

10

20

25

30

35

40

45

50

55

**[0053]** The 2-in-1 alkaline compositions according to the invention can further be combined with various functional components suitable for use in industrial ware wash applications. In some embodiments, the alkaline detergent and rinse aid compositions including the carbonate-based alkalinity source and nonionic surfactants (and/or polymers) make up a large amount or even substantially all of the total weight of the detergent composition. For example, in some embodiments few or no additional functional ingredients are disposed therein.

**[0054]** In other embodiments, additional functional ingredients may be included in the compositions. The functional ingredients provide desired properties and functionalities to the compositions. For the purpose of this application, the term "functional ingredient" includes a material that when dispersed or dissolved in a use and/or concentrate solution, such as an aqueous solution, provides a beneficial property in a particular use. Some particular examples of functional materials are discussed in more detail below, although the particular materials discussed are given by way of example only, and that a broad variety of other functional ingredients may be used. For example, many of the functional materials discussed below relate to materials used in cleaning, specifically ware wash applications. However, other embodiments may include functional ingredients for use in other applications.

**[0055]** In preferred embodiments, the compositions do not include additional alkalinity sources, namely alkali metal hydroxides. In further preferred embodiments, the compositions do not include rinse aids.

**[0056]** In other embodiments, the compositions may include builders, water conditioning agents, stabilizers, defoaming agents, anti-redeposition agents, bleaching agents, sanitizers, solubility modifiers, dispersants, anticorrosion agents and metal protecting agents, stabilizing agents, corrosion inhibitors, enzymes, additional sequestrants and/or chelating agents, fragrances and/or dyes, rheology modifiers or thickeners, hydrotropes or couplers, buffers, solvents, solidifying agents and the like.

### Builders

**[0057]** The alkaline detergent composition can include one or more building agents, also called chelating or sequestering agents (e.g. builders) to treat or soften water and to prevent formation of precipitates or other salts. These may include, but are not limited to: condensed phosphates, alkali metal carbonates, alkali metal silicates and metasilicates, phosphonates, aminocarboxylic acids, and/or polycarboxylic acid polymers. In general, a chelating agent is a molecule capable of coordinating (i.e., binding) the metal ions commonly found in natural water to prevent the metal ions from interfering with the action of the other detersive ingredients of a cleaning composition. Preferable levels of addition for builders that can also be chelating or sequestering agents are between about 0.1% to about 70% by weight, about 1% to about 60% by weight, about 5% to about 50% by weight, or about 20% to about 50% by weight. If the solid detergent is provided as a concentrate, the concentrate can include between approximately 1% to approximately 60% by weight,

between approximately 3% to approximately 50% by weight, and between approximately 6% to approximately 45% by weight of the builders. Additional ranges of the builders include between approximately 3% to approximately 20% by weight, between approximately 6% to approximately 15% by weight, and between approximately 25% to approximately 50% by weight. In addition, without being limited according to the invention, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

**[0058]** Examples of condensed phosphates include, but are not limited to: sodium and potassium orthophosphate, sodium and potassium pyrophosphate, sodium tripolyphosphate, and sodium hexametaphosphate. A condensed phosphate may also assist, to a limited extent, in solidification of the detergent composition by fixing the free water present in the composition as water of hydration. A preferred builder is sodium tripolyphosphate anhydrous.

[0059] Examples of phosphonates include, but are not limited to: 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), 1-hydroxyethane-1,1-diphosphonic acid,  $CH_2C(OH)[PO(OH)_2]_2$ ; aminotri(methylenephosphonic acid),  $N[CH_2PO(OH)_2]_3$ ; aminotri(methylenephosphonate), sodium salt (ATMP),  $N[CH_2PO(ONa)_2]_3$ ; 2-hydroxyethyliminobis(methylenephosphonic acid),  $HOCH_2CH_2N[CH_2PO(OH)_2]_2$ ; diethylenetriaminepenta(methylenephosphonic acid),  $(HO)_2POCH_2N[CH_2CH_2N[CH_2PO(OH)_2]_2]_2$ ; diethylenetriaminepenta(methylenephosphonate), sodium salt (DTPMP),  $C_9H_{(28-x)}N_3Na_xO_{15}P_5$  (x=7); hexamethylenediamine(tetramethylenephosphonate), potassium salt,  $C_{10}H_{(28-x)}N_2KxO_{12}P_4$  (x=6); bis(hexamethylene)triamine(pentamethylenephosphonic acid),  $(HO_2)POCH_2N[(CH_2)_2N[CH_2PO(OH)_2]_2]_2$ ; and phosphorus acid,  $H_3PO_3$ . A preferred phosphonate combination is ATMP and HEDP. A neutralized or alkali phosphonate, or a combination of the phosphonate with an alkali source prior to being added into the mixture such that there is little or no heat or gas generated by a neutralization reaction when the phosphonate is added is preferred. In one embodiment, however, the detergent composition is phosphorous-free.

**[0060]** Useful aminocarboxylic acid materials containing little or no NTA include, but are not limited to: N-hydroxyethyl-aminodiacetic acid, ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DT-PA), aspartic acid-N,N-diacetic acid (ASDA), methylglycinediacetic acid (MGDA), glutamic acid-N,N-diacetic acid (GLDA), ethylenediaminesuccinic acid (EDDS), 2-hydroxyethyliminodiacetic acid (HEDA), iminodisuccinic acid (IDS), 3-hydroxy-2-2'-iminodisuccinic acid (HIDS) and other similar acids or salts thereof having an amino group with a carboxylic acid substituent. In one embodiment, however, the composition is free of aminocarboxylates.

[0061] Water conditioning polymers can also be used as non-phosphorus containing builders. Exemplary water conditioning polymers include, but are not limited to: polycarboxylates. Exemplary polycarboxylates that can be used as builders and/or water conditioning polymers include, but are not limited to: those having pendant carboxylate (-CO<sub>2-</sub>) groups such as polyacrylic acid, maleic acid, maleic/olefin copolymer, sulfonated copolymer or terpolymer, acrylic/maleic copolymer, polymethacrylic acid, acrylic acid-methacrylic acid copolymers, hydrolyzed polyacrylamide, hydrolyzed polyamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, hydrolyzed polymethacrylonitrile, and hydrolyzed acrylonitrile-methacrylonitrile copolymers. Other suitable water conditioning polymers include starch, sugar or polyols comprising carboxylic acid or ester functional groups. Exemplary carboxylic acids include but are not limited to maleic, acrylic, methacrylic and itaconic acid or salts thereof. Exemplary ester functional groups include aryl, cyclic, aromatic and C<sub>1</sub>-C<sub>10</sub> linear, branched or substituted esters. For a further discussion of chelating agents/sequestrants, see Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, volume 5, pages 339-366 and volume 23, pages 319-320, the disclosure of which is incorporated by reference herein. These materials may also be used at substoichiometric levels to function as crystal modifiers.

## Water Conditioning Agents

10

15

30

35

40

45

50

55

[0062] The alkaline detergent compositions can include one or more water conditioning agents. In an aspect, phosphonic acids can be employed. Phosphonic acids can be used in the form of water soluble acid salts, particularly the alkali metal salts, such as sodium or potassium; the ammonium salts; or the alkylol amine salts where the alkylol has 2 to 3 carbon atoms, such as mono-, di-, or triethanolamine salts. Preferred phosphonates include the organic phosphonates. Preferred organic phosphonates include phosphono butane tricarboxylic acid (PBTC) available from Bayer Corp. in Pittsburgh Pa. under the tradename of BAYHIBIT™ and hydroxy ethylidene diphosphonic acid (HEDP) such as that sold under the tradename of DEQUEST ™2010 available from Monsanto Chemical Co. Additional description of suitable water conditioning agents for use in the invention is described in U.S. Patent No. 6,436,893, which is herein incorporated by reference herein in its entirety.

[0063] In an aspect, the compositions include from about 0.1 wt-% - 50 wt-% water conditioning agent, from about 1 wt-% - 40 wt-% water conditioning agent, from about 1 wt-% - 30 wt-% water conditioning agent, preferably from about 5 wt-% - 20 wt-% water conditioning agent. In addition, without being limited according to the invention, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

### Neutralizing Agents

[0064] The alkaline detergent compositions may also include a neutralizing agent. For example, in certain embodiments an alkaline neutralizing agent may be employed to neutralize acidic components, such as a water conditioning agent. Suitable alkaline neutralizing agents may include for example alkali metal hydroxides, including but not limited to: sodium hydroxide, potassium hydroxide, lithium hydroxide, and combinations thereof. An alkali metal hydroxide neutralizing agent may be added to the composition in any form known in the art, including as solid beads, dissolved in an aqueous solution, or a combination thereof. Additionally, more than one neutralizing agent may be used according to certain embodiments. In an aspect of the invention, the compositions of the invention do not include hydroxides as alkalinity sources but only to neutralize acidic ingredients in the composition, including for example water conditioning agents such as HEDP.

[0065] In an aspect, the compositions include from about 0.1 wt-% - 50 wt-% neutralizing agent, from about 0.1 wt-% - 30 wt-% neutralizing agent, from about 1 wt-% - 25 wt-% neutralizing agent, preferably from about 10 wt-% - 25 wt-% neutralizing agent. In an embodiment of the invention, the neutralizing agent comprises alkali metal hydroxide in an amount of up to about 10 wt-%, preferably between about 0.01 wt-% and about 10 wt-%. In addition, without being limited according to the invention, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

#### Anti-Etch Agents

10

15

20

30

35

40

45

50

[0066] The alkaline detergent compositions may also include an anti-etch agent capable of preventing etching in glass. Examples of suitable anti-etch agents include adding metal ions to the composition such as zinc, zinc chloride, zinc gluconate, aluminum, and beryllium. The corrosion inhibitor can refer to the combination of a source of aluminum ion and a source of zinc ion. The source of aluminum ion and the source of zinc ion provide aluminum ion and zinc ion, respectively, when the solid detergent composition is provided in the form of a use solution. The amount of the corrosion inhibitor is calculated based upon the combined amount of the source of aluminum ion and the source of zinc ion. Anything that provides an aluminum ion in a use solution can be referred to as a source of aluminum ion, and anything that provides a zinc ion when provided in a use solution can be referred to as a source of zinc ion. It is not necessary for the source of aluminum ion and/or the source of zinc ion to react to form the aluminum ion and/or the zinc ion. Aluminum ions can be considered a source of aluminum ion, and zinc ions can be considered a source of zinc ion. The source of aluminum ion and the source of zinc ion can be provided as organic salts, inorganic salts, and mixtures thereof. Exemplary sources of aluminum ion include, but are not limited to: aluminum salts such as sodium aluminate, aluminum bromide, aluminum chlorate, aluminum chloride, aluminum iodide, aluminum nitrate, aluminum sulfate, aluminum acetate, aluminum formate, aluminum tartrate, aluminum lactate, aluminum oleate, aluminum bromate, aluminum borate, a num potassium sulfate, aluminum zinc sulfate, and aluminum phosphate. Exemplary sources of zinc ion include, but are not limited to: zinc salts such as zinc chloride, zinc sulfate, zinc nitrate, zinc iodide, zinc thiocyanate, zinc fluorosilicate, zinc dichromate, zinc chlorate, sodium zincate, zinc gluconate, zinc acetate, zinc benzoate, zinc citrate, zinc lactate, zinc formate, zinc bromate, zinc bromide, zinc fluoride, zinc fluorosilicate, and zinc salicylate.

**[0067]** The composition preferably includes from about 0.001 wt-% to about 10 wt-%, more preferably from about 0.01 wt-% to about 7 wt-%, and most preferably from about 0.01 wt-% to about 1 wt-% of an anti-etch agent. In addition, without being limited according to the invention, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

## Anticorrosion Agents

**[0068]** The alkaline detergent compositions may optionally include an anticorrosion agent. Anticorrosion agents provide compositions that generate surfaces that are shinier and less prone to biofilm buildup than surfaces that are not treated with compositions having anticorrosion agents.

[0069] Preferred anticorrosion agents which can be used according to the invention include phosphonates, phosphonic acids, triazoles, organic amines, sorbitan esters, carboxylic acid derivatives, sarcosinates, phosphate esters, zinc, nitrates, chromium, molybdate containing components, and borate containing components. Exemplary phosphates or phosphonic acids are available under the name Dequest (i.e., Dequest 2000, Dequest 2006, Dequest 2010, Dequest 2016, Dequest 2054, Dequest 2060, and Dequest 2066) from Solutia, Inc. of St. Louis, Mo. Exemplary triazoles are available under the name Cobratec (i.e., Cobratec 100, Cobratec TT-50-S, and Cobratec 99) from PMC Specialties Group, Inc. of Cincinnati, Ohio. Exemplary organic amines include aliphatic amines, aromatic amines, monoamines, diamines, triamines, polyamines, and their salts. Exemplary amines are available under the names Amp (i.e. Amp-95) from Angus Chemical Company of Buffalo Grove, III.; WGS (i.e., WGS-50) from Jacam Chemicals, LLC of Sterling, Kans.; Duomeen (i.e., Duomeen O and Duomeen C) from Akzo Nobel Chemicals, Inc. of Chicago, III.; DeThox amine

(C Series and T Series) from DeForest Enterprises, Inc. of Boca Raton, Fla.; Deriphat series from Henkel Corp. of Ambler, Pa.; and Maxhib (AC Series) from Chemax, Inc. of Greenville, S.C. Exemplary sorbitan esters are available under the name Calgene (LA-series) from Calgene Chemical Inc. of Skokie, Ill. Exemplary carboxylic acid derivatives are available under the name Recor (i.e., Recor 12) from Ciba-Geigy Corp. of Tarrytown, N.Y. Exemplary sarcosinates are available under the names Hamposyl from Hampshire Chemical Corp. of Lexington, Mass.; and Sarkosyl from Ciba-Geigy Corp. of Tarrytown, N.Y.

**[0070]** The composition optionally includes an anticorrosion agent for providing enhanced luster to the metallic portions of a dish machine and/or providing shinier surfaces. When an anticorrosion agent is incorporated into the composition, it is preferably included in an amount of between about 0.01 wt-% and about 7.5 wt-%, between about 0.01 wt-% and about 5 wt-% and between about 0.01 wt-% and about 3 wt-%.

#### Antiredeposition Agents

**[0071]** The alkaline detergent compositions may also include an antiredeposition agent capable of facilitating sustained suspension of soils in a cleaning solution and preventing the removed soils from being redeposited onto the substrate being cleaned. Examples of suitable antiredeposition agents include fatty acid amides, complex phosphate esters, styrene maleic anhydride copolymers, and cellulosic derivatives such as hydroxyethyl cellulose, hydroxypropyl cellulose, and the like. The composition preferably includes from about 0.5 wt-% to about 10 wt-% and more preferably from about 1 wt-% to about 5 wt-% of an antiredeposition agent.

## Enzymes

15

20

30

35

40

45

50

55

**[0072]** The alkaline detergent compositions can include one or more enzymes, which can provide desirable activity for removal of protein-based, carbohydrate-based, or triglyceride-based soils from substrates such as flatware, cups and bowls, and pots and pans. Enzymes suitable for the inventive composition can act by degrading or altering one or more types of soil residues encountered on a surface thus removing the soil or making the soil more removable by a surfactant or other component of the cleaning composition. Both degradation and alteration of soil residues can improve detergency by reducing the physicochemical forces which bind the soil to the surface or textile being cleaned, i.e. the soil becomes more water soluble. For example, one or more proteases can cleave complex, macromolecular protein structures present in soil residues into simpler short chain molecules which are, of themselves, more readily desorbed from surfaces, solubilized, or otherwise more easily removed by detersive solutions containing said proteases.

[0073] Suitable enzymes include a protease, an amylase, a lipase, a gluconase, a cellulase, a peroxidase, or a mixture thereof of any suitable origin, such as vegetable, animal, bacterial, fungal or yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases. In some embodiments preferably the enzyme is a protease, a lipase, an amylase, or a combination thereof. A valuable reference on enzymes, which is incorporated herein by reference is "Industrial Enzymes," Scott, D., in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, (editors Grayson, M. and EcKroth, D.) Vol. 9, pp. 173-224, John Wiley & Sons, New York, 1980.

**[0074]** In embodiments employing an enzyme the composition preferably includes from about 0.001 wt-% to about 10 wt-%, from about 0.01 wt-% to about 10 wt-%, from about 0.05 wt-% to about 5 wt-%, and more preferably from about 0.1 wt-% to about 1 wt-% of enzyme(s).

## Antimicrobial Agent

[0075] The alkaline detergent compositions may optionally include an antimicrobial agent or preservative. Antimicrobial agents are chemical compositions that can be used in the composition to prevent microbial contamination and deterioration of commercial products material systems, surfaces, etc. Antimicrobial agents may also be sanitizing agents. Generally, these materials fall in specific classes including phenolics, halogen compounds, quaternary ammonium compounds, metal derivatives, amines, alkanol amines, nitro derivatives, analides, organosulfur and sulfur-nitrogen compounds and miscellaneous compounds. The given antimicrobial agent depending on chemical composition and concentration may simply limit further proliferation of numbers of the microbe or may destroy all or a substantial proportion of the microbial population. The terms "microbes" and "microorganisms" typically refer primarily to bacteria and fungus microorganisms. In use, the antimicrobial agents are formed into the final product that when diluted and dispensed using an aqueous stream forms an aqueous disinfectant or sanitizer composition that can be contacted with a variety of surfaces resulting in prevention of growth or the killing of a substantial proportion of the microbial population. Common antimicrobial agents that may be used include phenolic antimicrobials such as pentachlorophenol, orthophenylphenol; halogen containing antibacterial agents that may be used include sodium trichloroisocyanurate, sodium dichloroisocy-

anurate (anhydrous or dihydrate), iodine-poly(vinylpyrolidin-onen) complexes, bromine compounds such as 2-bromo-2-nitropropane-1,3-diol; quaternary antimicrobial agents such as benzalconium chloride, cetylpyridiniumchloride; amines and nitro containing antimicrobial compositions such as hexahydro-1,3,5-tris(2-hydr- oxyethyl)-s-triazine, dithiocarbamates such as sodium dimethyldithiocarbamate, and a variety of other materials known in the art for their microbial properties. Antimicrobial agents may be encapsulated to improve stability and/or to reduce reactivity with other materials in the detergent composition.

**[0076]** When an antimicrobial agent or preservative is incorporated into the composition, it is preferably included in an amount between about 0.01 wt-% to about 5 wt-%, between about 0.01 wt-% to about 2 wt-%, and between about 0.1 wt-% to about 1.0 wt-%.

#### Foam Inhibitors

10

15

20

25

30

35

40

45

50

**[0077]** A foam inhibitor may be included in addition to the nonionic surfactants of the alkaline cleaning compositions for reducing the stability of any foam that is formed. Examples of foam inhibitors include silicon compounds such as silica dispersed in polydimethylsiloxane, fatty amides, hydrocarbon waxes, fatty acids, fatty esters, fatty alcohols, fatty acid soaps, ethoxylates, mineral oils, polyethylene glycol esters, polyoxyethylene-polyoxypropylene block copolymers, alkyl phosphate esters such as monostearyl phosphate and the like. A discussion of foam inhibitors may be found, for example, in U.S. Pat. No. 3,048,548 to Martin et al., U.S. Pat. No. 3,334,147 to Brunelle et al., and U.S. Pat. No. 3,442,242 to Rue et al., the disclosures of which are incorporated by reference herein. The composition preferably includes from about 0.0001 wt-% to about 5 wt-% and more preferably from about 0.01 wt-% to about 3 wt-% of the foam inhibitor.

#### Additional Surfactants

[0078] The compositions of invention may include additional surfactants. Particularly suitable surfactants include nonionic surfactants, amphoteric surfactants, and zwitterionic surfactants. In a preferred embodiment the compositions are substantially free of cationic and/or anionic surfactants. In an aspect, the compositions can include from about 0.01 wt-% - 40 wt-% additional surfactants, preferably from about 0.1 wt-% - 30 wt-% additional surfactant, more preferably from about 1 wt-% - 25 wt-% additional surfactant. In addition, without being limited according to the invention, all ranges recited are inclusive of the numbers defining the range and include each integer within the defined range.

## Nonionic Surfactants

**[0079]** Suitable nonionic surfactants suitable for use with the compositions of the present invention include alkoxylated surfactants. Suitable alkoxylated surfactants include EO/PO copolymers, capped EO/PO copolymers, alcohol alkoxylates, capped alcohol alkoxylates, mixtures thereof, or the like. Suitable alkoxylated surfactants for use as solvents include EO/PO block copolymers, such as the Pluronic and reverse Pluronic surfactants; alcohol alkoxylates, such as Dehypon LS-54 (R-(EO) $_5$ (PO) $_4$ ) and Dehypon LS-36 (R-(EO) $_3$ (PO) $_6$ ); and capped alcohol alkoxylates, such as Plurafac LF221 and Tegoten EC 11; mixtures thereof, or the like.

**[0080]** The semi-polar type of nonionic surface active agents is another class of nonionic surfactant useful in compositions of the present invention. Semi-polar nonionic surfactants include the amine oxides, phosphine oxides, sulfoxides and their alkoxylated derivatives.

[0081] Amine oxides are tertiary amine oxides corresponding to the general formula:

$$R^{1} \longrightarrow (OR^{4})_{n} \longrightarrow N \longrightarrow O$$

$$\downarrow R^{3}$$

wherein the arrow is a conventional representation of a semi-polar bond; and,  $R^1$ ,  $R^2$ , and  $R^3$  may be aliphatic, aromatic, heterocyclic, alicyclic, or combinations thereof. Generally, for amine oxides of detergent interest,  $R^1$  is an alkyl radical of from about 8 to about 24 carbon atoms;  $R^2$  and  $R^3$  are alkyl or hydroxyalkyl of 1-3 carbon atoms or a mixture thereof;  $R^2$  and  $R^3$  can be attached to each other, e.g. through an oxygen or nitrogen atom, to form a ring structure;  $R^4$  is an alkylene or a hydroxyalkylene group containing 2 to 3 carbon atoms; and n ranges from 0 to about 20. An amine oxide can be generated from the corresponding amine and an oxidizing agent, such as hydrogen peroxide.

[0082] Useful water soluble amine oxide surfactants are selected from the octyl, decyl, dodecyl, isododecyl, coconut,

or tallow alkyl di-(lower alkyl) amine oxides, specific examples of which are octyldimethylamine oxide, nonyldimethylamine oxide, decyldimethylamine oxide, undecyldimethylamine oxide, dodecyldimethylamine oxide, iso-dodecyldimethylamine oxide, tridecyldimethylamine oxide, tetradecyldimethylamine oxide, pentadecyldimethylamine oxide, hexadecyldimethylamine oxide, octadecyldimethylamine oxide, dodecyldipropylamine oxide, tetradecyldipropylamine oxide, tetradecyldipropylamine oxide, octadecyldibutylamine oxide, octadecyldibutylamine oxide, bis(2-hydroxyethyl)dodecylamine oxide, bis(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, 3,6,9-trioctadecyldimethylamine oxide and 3-dodecoxy-2-hydroxypropyldi-(2-hydroxyethyl)amine oxide.

### 10 Amphoteric Surfactants

15

20

25

30

45

50

55

**[0083]** Amphoteric, or ampholytic, surfactants contain both a basic and an acidic hydrophilic group and an organic hydrophobic group. These ionic entities may be any of anionic or cationic groups described herein for other types of surfactants. A basic nitrogen and an acidic carboxylate group are the typical functional groups employed as the basic and acidic hydrophilic groups. In a few surfactants, sulfonate, sulfate, phosphonate or phosphate provide the negative charge.

**[0084]** Amphoteric surfactants can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, *e.g.*, carboxy, sulfo, sulfato, phosphate, or phosphono. Amphoteric surfactants are subdivided into two major classes known to those of skill in the art and described in "Surfactant Encyclopedia" Cosmetics & Toiletries, Vol. 104 (2) 69-71 (1989), which is herein incorporated by reference in its entirety. The first class includes acyl/dialkyl ethylenediamine derivatives (*e.g.* 2-alkyl hydroxyethyl imidazoline derivatives) and their salts. The second class includes N-alkylamino acids and their salts. Some amphoteric surfactants can be envisioned as fitting into both classes.

**[0085]** Amphoteric surfactants can be synthesized by methods known to those of skill in the art. For example, 2-alkyl hydroxyethyl imidazoline is synthesized by condensation and ring closure of a long chain carboxylic acid (or a derivative) with dialkyl ethylenediamine. Commercial amphoteric surfactants are derivatized by subsequent hydrolysis and ring-opening of the imidazoline ring by alkylation — for example with chloroacetic acid or ethyl acetate. During alkylation, one or two carboxy-alkyl groups react to form a tertiary amine and an ether linkage with differing alkylating agents yielding different tertiary amines.

[0086] Long chain imidazole derivatives having application in the present invention generally have the general formula:

Neutral pH - Zwitterion

wherein R is an acyclic hydrophobic group containing from about 8 to 18 carbon atoms and M is a cation to neutralize the charge of the anion, generally sodium. Commercially prominent imidazoline-derived amphoterics that can be employed in the present compositions include for example: Cocoamphopropionate, Cocoamphocarboxypropionate, Cocoamphoglycinate, Cocoamphocarboxy-glycinate, Cocoamphopropylsulfonate, and Cocoamphocarboxy-propionic acid. Amphocarboxylic acids can be produced from fatty imidazolines in which the dicarboxylic acid functionality of the amphodicarboxylic acid is diacetic acid and/or dipropionic acid.

[0087] The carboxymethylated compounds (glycinates) described herein above frequently are called betaines. Betaines are a special class of amphoteric discussed herein below in the section entitled, Zwitterion Surfactants.

[0088] Long chain N-alkylamino acids are readily prepared by reaction RNH $_2$ , in which R=C $_8$ -C $_{18}$  straight or branched chain alkyl, fatty amines with halogenated carboxylic acids. Alkylation of the primary amino groups of an amino acid leads to secondary and tertiary amines. Alkyl substituents may have additional amino groups that provide more than one reactive nitrogen center. Most commercial N-alkylamine acids are alkyl derivatives of beta-alanine or beta-N(2-carboxyethyl) alanine. Examples of commercial N-alkylamino acid ampholytes having application in this invention include alkyl beta-amino dipropionates, RN(C $_2$ H $_4$ COOM) $_2$  and RNHC $_2$ H $_4$ COOM. In an embodiment, R can be an acyclic hydrophobic group containing from about 8 to about 18 carbon atoms, and M is a cation to neutralize the charge of the anion.

[0089] Suitable amphoteric surfactants include those derived from coconut products such as coconut oil or coconut fatty acid. Additional suitable coconut derived surfactants include as part of their structure an ethylenediamine moiety, an alkanolamide moiety, an amino acid moiety, e.g., glycine, or a combination thereof; and an aliphatic substituent of from about 8 to 18 (e.g., 12) carbon atoms. Such a surfactant can also be considered an alkyl amphodicarboxylic acid. These amphoteric surfactants can include chemical structures represented as:  $C_{12}$ -alkyl-C(O)-NH- $CH_2$ - $CH_2$ - $N^+(CH_2$ - $CO_2Na)_2$ - $CH_2$ - $CH_2$ -OH or  $C_{12}$ -alkyl-C(O)-N(H)- $CH_2$ - $CH_2$ - $N^+(CH_2$ - $CO_2Na)_2$ - $CH_2$ -OH. Disodium cocoampho dipropionate is one suitable amphoteric surfactant and is commercially available under the tradename Miranol TFBS from Rhodia Inc., Cranbury, N.J. Another suitable coconut derived amphoteric surfactant with the chemical name disodium cocoampho diacetate is sold under the tradename Mirataine JCHA, also from Rhodia Inc., Cranbury, N.J.

**[0090]** A typical listing of amphoteric classes, and species of these surfactants, is given in U.S. Pat. No. 3,929,678 issued to Laughlin and Heuring on Dec. 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch).

### Zwitterionic Surfactants

5

10

15

20

30

35

**[0091]** Zwitterionic surfactants can be thought of as a subset of the amphoteric surfactants and can include an anionic charge. Zwitterionic surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Typically, a zwitterionic surfactant includes a positive charged quaternary ammonium or, in some cases, a sulfonium or phosphonium ion; a negative charged carboxyl group; and an alkyl group. Zwitterionics generally contain cationic and anionic groups which ionize to a nearly equal degree in the isoelectric region of the molecule and which can develop strong" inner-salt" attraction between positive-negative charge centers. Examples of such zwitterionic synthetic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, *e.g.*, carboxy, sulfonate, phosphate, or phosphonate.

**[0092]** Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein. A general formula for these compounds is:

$$(R^2)_X$$
 $|_{+}$ 
 $R^1-Y-CH_2-R-Z$ 

wherein  $R^1$  contains an alkyl, alkenyl, or hydroxyalkyl radical of from 8 to 18 carbon atoms having from 0 to 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^2$  is an alkyl or monohydroxy alkyl group containing 1 to 3 carbon atoms; x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom,  $R^3$  is an alkylene or hydroxy alkylene or hydroxy alkylene of from 1 to 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

[0093] Examples of zwitterionic surfactants having the structures listed above include: 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate; 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate; 3-[P,P-diethyl-P-3,6,9-trioxatetracosanephosphonio]-2-hydroxypropane-1-phosphate; 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropyl-ammonio]-propane-1-phosphonate; 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy-propane-1-sulfonate; 4-[N,N-di(2(2-hydroxyethyl)-N(2-hydroxydodecyl)ammonio]-butane-1-carboxylate; 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate; 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and S[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate. The alkyl groups contained in said detergent surfactants can be straight or branched and saturated or unsaturated.

[0094] The zwitterionic surfactant suitable for use in the present compositions includes a betaine of the general structure:

These surfactant betaines typically do not exhibit strong cationic or anionic characters at pH extremes nor do they show reduced water solubility in their isoelectric range. Unlike "external" quaternary ammonium salts, betaines are compatible with anionics. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine;  $C_{12-14}$  acylamidopropylbetaine;  $C_{8-14}$  acylamidohexyldiethyl betaine;  $4-C_{14-16}$  acylamidodiethylamidodiethylamidodimethylbetaine;  $C_{12-16}$  acylamidopentanediethylbetaine; and  $C_{12-16}$  acylamidodimethylbetaine.

**[0095]** Sultaines useful in the present invention include those compounds having the formula  $(R(R^1)_2 N^+ R^2SO^{3-}, in Which R is a C_6 - C_{18}$  hydrocarbyl group, each  $R^1$  is typically independently  $C_1 - C_3$  alkyl, e.g. methyl, and  $R^2$  is a  $C_1 - C_6$  hydrocarbyl group, e.g. a  $C_1 - C_3$  alkylene or hydroxyalkylene group.

**[0096]** A typical listing of zwitterionic classes, and species of these surfactants, is given in U.S. Pat. No. 3,929,678 issued to Laughlin and Heuring on Dec. 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). Each of these references is herein incorporated in their entirety.

**[0097]** In an embodiment, the compositions of the present invention include a betaine. For example, the compositions can include cocoamido propyl betaine.

#### **Embodiments**

5

10

15

20

25

30

35

40

45

50

55

[0098] Exemplary ranges of the 2-in-1 alkaline detergent compositions according to the invention are shown in Tables 1A and 1B in weight percentage of the solid detergent compositions.

TABLE 1A

Material	First Exemplary Range wt-%	Second Exemplary Range wt-%	Third Exemplary Range wt-%	Fourth Exemplary Range wt-%
Alkalinity Source	10-95	25-90	40-85	45-75
Builders	0.1-50	1-50	5-45	10-35
Surfactants	0.01-30	0. 1-25	0.1-20	1-10
Additional Functional Ingredients	0-40	0-30	0-25	0-20

TABLE 1B

Material	First Exemplary Range wt-%	Second Exemplary Range wt-%	Third Exemplary Range wt-%	Fourth Exemplary Range wt-%
Alkalinity Source	10-95	25-90	40-85	45-75
Polymer	0.1-50	0.1-40	0.1-30	1-20
Builders	0.1-50	1-50	5-45	10-35
Surfactants	0.1-30	0.1-25	0.1-20	1-10
Additional Functional Ingredients	0-40	0-30	0-25	0-20

**[0099]** The detergent compositions may include concentrate compositions or may be diluted to form use compositions. In general, a concentrate refers to a composition that is intended to be diluted with water to provide a use solution that contacts an object to provide the desired cleaning, rinsing, or the like. The detergent composition that contacts the articles to be washed can be referred to as a concentrate or a use composition (or use solution) dependent upon the formulation employed in methods according to the invention. It should be understood that the concentration of the

aminocarboxylate, water conditioning agent, alkalinity, water and other optional functional ingredients in the detergent composition will vary depending on whether the detergent composition is provided as a concentrate or as a use solution. **[0100]** A use solution may be prepared from the concentrate by diluting the concentrate with water at a dilution ratio that provides a use solution having desired detersive properties. The water that is used to dilute the concentrate to form the use composition can be referred to as water of dilution or a diluent, and can vary from one location to another. The typical dilution factor is between approximately 1 and approximately 10,000 but will depend on factors including water hardness, the amount of soil to be removed and the like. In an embodiment, the concentrate is diluted at a ratio of between about 1:10 and about 1:10,000 concentrate to water. Particularly, the concentrate is diluted at a ratio of between about 1:2,000 concentrate to water. More particularly, the concentrate is diluted at a ratio of between about 1:2,000 concentrate to water.

Method of Use - Cleaning an Article in a Dish Machine

10

15

20

30

35

40

50

55

**[0101]** In an embodiment, methods of the present invention involve using the steps of providing an alkaline 2-in-1 detergent composition as disclosed herein. In particular, methods of use preferably employ a solid alkaline 2-in-1 detergent composition, wherein a solid composition is inserted into a dispenser in or associated with an dish machine, particularly an industrial warewash machine. In an embodiment of the invention, the solid composition may be provided as a multipleuse dosage having between about 10 and about 10,000 doses per solid composition. In another aspect of the invention, the solid composition can be formulated in a single-use composition, where it is used one time in a wash. The methods also include forming a wash solution with the alkaline 2-in-1 detergent composition and water, contacting a soil on an article in the dish machine with the wash solution, removing the soil, and rinsing the article with potable water without requiring the use of a separate rinse aid composition. The rinse is with potable water only.

**[0102]** In another embodiment, the methods of the present invention may involve providing the individual components of the 2-in-1 detergent composition separately and mixing the individual components in situ with water to form a desired wash solution.

[0103] When carrying out the methods of the invention, the 2-in-1 detergent compositions described above are inserted into a dispenser of a dish machine. The dispenser may be selected from a variety of different dispensers depending of the physical form of the composition. For example, a liquid composition may be dispensed using a pump, either peristaltic or bellows for example, syringe/plunger injection, gravity feed, siphon feed, aspirators, unit dose, for example using a water soluble packet such as polyvinyl alcohol, or a foil pouch, evacuation from a pressurized chamber, or diffusion through a membrane or permeable surface. If the composition is a gel or a thick liquid, it may be dispensed using a pump such as a peristaltic or bellows pump, syringe/plunger injection, caulk gun, unit dose, for example using a water soluble packet such as polyvinyl alcohol or a foil pouch, evacuation from a pressurized chamber, or diffusion through a membrane or permeable surface. Preferably, when the composition is a solid or powder, the composition may be dispensed using a spray, flood, auger, shaker, tablet-type dispenser, unit dose using a water soluble packet such as polyvinyl alcohol or foil pouch, or diffusion through a membrane or permeable surface. The dispenser may also be a dual dispenser in which one component, is dispensed on one side and another component is dispensed on another side. These exemplary dispensers may be located in or associated with a variety of dish machines including under the counter dish machines, bar washers, door machines, conveyor machines, or flight machines. The dispenser may be located inside the dish machine, remote, or mounted outside of the dishwasher. A single dispenser may feed one or more dish machines.

**[0104]** Once the 2-in-1 detergent composition is inserted into the dispenser, the wash cycle of the dish machine is started and a wash solution is formed. The wash solution comprises the alkaline 2-in-1 detergent composition and water from the dish machine. The water may be any type of water including hard water, soft water, clean water, or dirty water. The most preferred wash solution is one that maintains the preferred pH ranges of about 7 to about 11.5, more preferably about 9.5 to about 11.5, as measured by a pH probe based on a solution of the composition in a 16 gallon dish machine. The same probe may be used to measure millivolts if the probe allows for both functions, simply by switching the probe from pH to millivolts. The dispenser or the dish machine may optionally include a pH probe to measure the pH of the wash solution throughout the wash cycle. The actual concentration or water to detergent ratio depends on the particular surfactant used. Exemplary concentration ranges may include up to 3000 ppm, preferably 1 to 3000 ppm, more preferably 100 to 3000 ppm and most preferably 300 to 2000 ppm. Again, the actual concentration used depends on the surfactant chosen.

**[0105]** A use solution can have an elevated temperature (i.e. heated to an elevated temperature when used according to the methods of the invention. In one example, a use solution having a temperature between approximately 120°F and about 185°F, between about 140°F and approximately 185°F is contacted with the substrate to be cleaned. In another example, a use solution having a temperature between approximately 150°F and approximately 160°F is contacted with the substrate to be cleaned.

[0106] After the wash solution is formed, the wash solution contacts a soil on an article in the dish machine. Examples

of soils include soils typically encountered with food such as proteinaceous soils, hydrophobic fatty soils, starchy and sugary soils associated with carbohydrates and simple sugars, soils from milk and dairy products, fruit and vegetable soils, and the like. Soils can also include minerals, from hard water for example, such as potassium, calcium, magnesium, and sodium. Articles that may be contacted include articles made of glass, plastic, aluminum, steel, copper, brass, silver, rubber, wood, ceramic, and the like. Articles include things typically found in a dish machine such as glasses, bowls, plates, cups, pots and pans, bakeware such as cookie sheets, cake pans, muffin pans etc., silverware such as forks, spoons, knives, cooking utensils such as wooden spoons, spatulas, rubber scrapers, utility knives, tongs, grilling utensils, serving utensils, etc. The wash solution may contact the soil in a number of ways including spraying, dipping, sump-pump solution, misting and fogging.

**[0107]** Once the wash solution has contacted the soil, the soil is removed from the article. The removal of the soil from the article is accomplished by the chemical reaction between the wash solution and the soil as well as the mechanical action of the wash solution on the article depending on how the wash solution is contacting the article.

**[0108]** Once the soil is removed, the articles are rinsed as part of the dish machine wash cycle employing potable water without the use of a separate or additional rinse aid composition.

**[0109]** The methods can include more steps or fewer steps than laid out here. For example, the method can include additional steps normally associated with a dish machine wash cycle. For example, the method can also optionally include the use of an acidic detergent. For example, the method can optionally include alternating the acidic detergent with an alkaline detergent as described.

## 20 Method of Manufacturing the Composition

10

30

35

40

50

55

**[0110]** The compositions of the present invention may include liquid products, thickened liquid products, gelled liquid products, paste, granular and pelletized solid compositions, powders, solid block compositions, extruded solid block composition and others.

**[0111]** Solid particulate materials can be made by merely blending the dry solid ingredients in appropriate ratios or agglomerating the materials in appropriate agglomeration systems. Pelletized materials can be manufactured by compressing the solid granular or agglomerated materials in appropriate pelletizing equipment to result in appropriately sized pelletized materials. Solid block and cast solid block materials can be made by introducing into a container either a prehardened block of material or a castable liquid that hardens into a solid block within a container. Preferred containers include disposable plastic containers or water soluble film containers. Other suitable packaging for the composition includes flexible bags, packets, shrink wrap, and water soluble film such as polyvinyl alcohol.

**[0112]** The solid detergent compositions may be formed using a batch or continuous mixing system. In an exemplary embodiment, a single- or twin-screw extruder is used to combine and mix one or more components at high shear to form a homogeneous mixture. In some embodiments, the processing temperature is at or below the melting temperature of the components. The processed mixture may be dispensed from the mixer by forming, casting or other suitable means, whereupon the detergent composition hardens to a solid form. The structure of the matrix may be characterized according to its hardness, melting point, material distribution, crystal structure, and other like properties according to known methods in the art. Generally, a solid detergent composition processed according to the method of the invention is substantially homogeneous with regard to the distribution of ingredients throughout its mass and is dimensionally stable.

[0113] In an extrusion process, the liquid and solid components are introduced into final mixing system and are continuously mixed until the components form a substantially homogeneous semi-solid mixture in which the components are distributed throughout its mass. The mixture is then discharged from the mixing system into, or through, a die or other shaping means. The product is then packaged. In an exemplary embodiment, the formed composition begins to harden to a solid form in between approximately 1 minute and approximately 3 hours. Particularly, the formed composition begins to harden to a solid form in between approximately 1 minute and approximately 2 hours. More particularly, the formed composition begins to harden to a solid form in between approximately 1 minute and approximately 20 minutes. [0114] In a casting process, the liquid and solid components are introduced into the final mixing system and are continuously mixed until the components form a substantially homogeneous liquid mixture in which the components are distributed throughout its mass. In an exemplary embodiment, the components are mixed in the mixing system for at least approximately 60 seconds. Once the mixing is complete, the product is transferred to a packaging container where solidification takes place. In an exemplary embodiment, the cast composition begins to harden to a solid form in between approximately 1 minute and approximately 3 hours. Particularly, the cast composition begins to harden to a solid form in between approximately 1 minute and approximately 2 hours. More particularly, the cast composition begins to harden to a solid form in between approximately 1 minute and approximately 2 hours. More particularly, the cast composition begins to harden to a solid form in between approximately 1 minute and approximately 2 hours. More particularly, the cast composition begins to harden to a solid form in between approximately 1 minute and approximately 2 hours.

**[0115]** In a pressed solid process, a flowable solid, such as granular solids or other particle solids including binding agents (e.g. hydrated chelating agent, such as a hydrated aminocarboxylate, a hydrated polycarboxylate or hydrated anionic polymer, a hydrated citrate salt or a hydrated tartrate salt, or the like together with an alkali metal carbonate) are combined under pressure. In a pressed solid process, flowable solids of the compositions are placed into a form

(e.g., a mold or container). The method can include gently pressing the flowable solid in the form to produce the solid cleaning composition. Pressure may be applied by a block machine or a turntable press, or the like. Pressure may be applied at about 1 to about 2000 psi, about 1 to about 300 psi, about 5 psi to about 2000 psi, or about 10 psi to about 100 psi. In certain embodiments, the methods can employ pressures as low as greater than or equal to about 1 psi, greater than or equal to about 2, greater than or equal to about 5 psi, or greater than or equal to about 10 psi. As used herein, the term "psi" or "pounds per square inch" refers to the actual pressure applied to the flowable solid being pressed and does not refer to the gauge or hydraulic pressure measured at a point in the apparatus doing the pressing. The method can include a curing step to produce the solid cleaning composition. As referred to herein, an uncured composition including the flowable solid is compressed to provide sufficient surface contact between particles making up the flowable solid that the uncured composition will solidify into a stable solid cleaning composition. A sufficient quantity of particles (e.g. granules) in contact with one another provides binding of particles to one another effective for making a stable solid composition. Inclusion of a curing step may include allowing the pressed solid to solidify for a period of time, such as a few hours, or about 1 day (or longer). In additional aspects, the methods could include vibrating the flowable solid in the form or mold, such as the methods disclosed in U.S. Patent No. 8,889,048, which is herein incorporated by reference in its entirety.

**[0116]** The use of pressed solids provide numerous benefits over conventional solid block or tablet compositions requiring high pressure in a tablet press, or casting requiring the melting of a composition consuming significant amounts of energy, and/or by extrusion requiring expensive equipment and advanced technical know-how. Pressed solids overcome such various limitations of other solid formulations for which there is a need for making solid cleaning compositions. Moreover, pressed solid compositions retain its shape under conditions in which the composition may be stored or handled.

[0117] By the term "solid", it is meant that the hardened composition will not flow and will substantially retain its shape under moderate stress or pressure or mere gravity. A solid may be in various forms such as a powder, a flake, a granule, a pellet, a tablet, a lozenge, a puck, a briquette, a brick, a solid block, a unit dose, or another solid form known to those of skill in the art. The degree of hardness of the solid cast composition and/or a pressed solid composition may range from that of a fused solid product which is relatively dense and hard, for example, like concrete, to a consistency characterized as being a hardened paste. In addition, the term "solid" refers to the state of the detergent composition under the expected conditions of storage and use of the solid detergent composition. In general, it is expected that the detergent composition will remain in solid form when exposed to temperatures of up to approximately 100°F and particularly up to approximately 120°F.

**[0118]** The resulting solid detergent composition may take forms including, but not limited to: a cast solid product; an extruded, molded or formed solid pellet, block, tablet, powder, granule, flake; pressed solid; or the formed solid can thereafter be ground or formed into a powder, granule, or flake. In an exemplary embodiment, extruded pellet materials formed by the solidification matrix have a weight of between approximately 50 grams and approximately 250 grams, extruded solids formed by the composition have a weight of approximately 100 grams or greater, and solid block detergents formed by the composition have a mass of between approximately 1 and approximately 10 kilograms. The solid compositions provide for a stabilized source of functional materials. In some embodiments, the solid composition may be dissolved, for example, in an aqueous or other medium, to create a concentrated and/or use solution. The solution may be directed to a storage reservoir for later use and/or dilution, or may be applied directly to a point of use.

**[0119]** The following patents disclose various combinations of solidification, binding and/or hardening agents that can be utilized in the solid cleaning compositions of the present invention. The following U.S. patents are incorporated herein by reference: U.S. Pat. Nos. 7,153,820; 7,094,746; 7,087,569; 7,037,886; 6,831,054; 6,730,653; 6,660,707; 6,653,266; 6,583,094; 6,410,495; 6,258,765; 6,177,392; 6,156,715; 5,858,299; 5,316,688; 5,234,615; 5,198,198; 5,078,301; 4,595,520; 4,680,134; RE32,763; and RE32818.

**[0120]** Liquid compositions can typically be made by forming the ingredients in an aqueous liquid or aqueous liquid solvent system. Such systems are typically made by dissolving or suspending the active ingredients in water or in compatible solvent and then diluting the product to an appropriate concentration, either to form a concentrate or a use solution thereof. Gelled compositions can be made similarly by dissolving or suspending the active ingredients in a compatible aqueous, aqueous liquid or mixed aqueous organic system including a gelling agent at an appropriate concentration.

**[0121]** All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated as incorporated by reference.

### **EXAMPLES**

10

15

20

30

35

45

50

55

[0122] Embodiments of the present invention are further defined in the following nonlimiting Examples. It should be

understood that these Examples, while indicating certain embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the embodiments of the invention to adapt it to various usages and conditions. Thus, various modifications of the embodiments of the invention, in addition to those shown and described herein, will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

### **EXAMPLES 1-4**

20

25

30

35

45

50

55

10 **[0123]** The materials used in the Examples 1-4 are provided herein:

Pluronic® 25R2: an EO/PO copolymer available from BASF. Novel® II 1012GB-21: an alcohol alkoxylate available from Sasol.

[0124] Additional materials commercially-available from multiple sources include: sodium carbonate, ash monohydrate, sodium tripolyphosphate (anhydrous), zinc chloride, HEDP, and KOH.

**[0125]** For Examples 1-4, an exemplary 2-in-1 detergent was prepared and is shown in Table 2. Throughout Examples 1-4, the formulation is referred to as Experimental Formula 1 (Exp. 1).

TABLE 2

Raw material	Exp. 1
Alkalinity source	45-75
Builder	10-30
Alkyl alkoxylate (EO/PO copolymer)	1-10
Alcohol alkoxylate	1-10
Sanitizing agent	1-10
Corrosion inhibitor	0.01-0.5
Phosphonate builder, 60%	1-10
KOH, 45%	1-10
Total	100

**[0126]** Existing detergents, rinse aids, and Experimental Formula 1 were tested against distilled water. Detergent Control 1 and Detergent Control 2 are commercially available detergents (phosphate-based detergents). Rinse Aid Control 1 and Rinse Aid Control 2 are two commercially available rinse aids (employing higher amounts of active ingredients and surfactants of at least two ionic categories (e.g. nonionic and cationic)). The use concentrations for all experiments described below are provided in the following table:

TABLE 3

Sample	Use concentration [ppm]				
DI water	N/A				
Detergent Control 1	1500				
Detergent Control 2	1000				
Rinse Aid Control 1	536				
Rinse Aid Control 2	536				
Exp. 1	1415				
1					

**[0127]** All warewash testing was performed with 10 oz. Libbey glasses on a Hobart AM-15 warewash machine. The specifications of the Hobart AM-15 warewash machine are as follows: Hobart AM-15 warewash machine specifications.

Washbath volume:	53L
Rinse volume:	2.8L
Wash time:	50 sec.
Rinse time:	9 sec.

## **EXAMPLE 1**

5

10

15

20

25

#### DYNAMIC SURFACE TENSION

**[0128]** The SITA science line t60 measures the dynamic surface tension of liquids up to the semi-static range. Air bubbles are generated from a capillary with known radius. The bubble pressure is measured as a function of bubble life time, which can be correlated to the surface tension according to the Young-Laplace equation. Dynamic surface tension provides insight into the dynamic behavior of surfactants and other surface active compounds under dynamic conditions, i.e. how quick surfactants can reach a surface. The dynamic surface tension is a function of concentration, temperature and type of surfactant. The dynamic surface tension behavior of surfactants is particularly important in applications where a quick response of surfactants is required, for example, in the short rinse cycles of automated dishwashing.

### APPARATUS AND MATERIALS:

## [0129]

- 7. SITA T60 (Sita Messtechnik, Germany)
- 8. Oil bath with stir bar
- 9. Heating and stirring plate
- 10. Glass beakers
- 11. Glass vials (20 mL)

30

[0130] The SITA science line t60 was calibrated with DI water. Clean water samples after calibration should have a surface tension of  $72.0\pm1.0$ mN/m (depending on water quality and temperature). Following calibration, the SITA was programmed to take readings at the desired time intervals (i.e., 0.3, 1.6, 3.0, and 9.1 seconds). Three separate solutions at the desired ppm were prepared for each composition (described as Samples A-C) to be tested (e.g., three samples of Exp. 1, three samples of Detergent Control 1). 10-15 mL were transferred into 20 mL vials and immersed in a heated oil bath to 72 °C (160 °F)  $\pm$  2°C. The samples were equilibrated for 10-15 minutes. The samples were individually removed from the oil bath and the tested in the SITA. After each sample was tested the SITA's cleaning procedure was run, then the surface tension of DI water was checked to ensure the SITA was adequately clean. If the DI water measurements were not within  $72.0 \pm 1.0$  mN/m, then the cleaning procedure was run again. The surface tension (mN/m) versus bubble life time at 160 °F experimental data is provided in Tables 4A through 4F below, wherein  $\tau$ : bubble life time (s);  $\gamma$ : surface tension (mN/m).

#### **TABLE 4A**

45

40

50

	Detergent Control 1						
Samp	le A	Samp	le B	Samp	le C		
τ	γ	τ	γ	τ	γ		
0.031	65.1	0.031	67.9	0.03	66.4		
0.041	65	0.042	65.9	0.041	66.2		
0.058	64.5	0.058	65.8	0.058	65		
0.083	64.1	0.082	65.3	0.081	64.1		
0.116	63.4	0.116	64.6	0.116	64.4		
0.159	62.8	0.161	63.8	0.162	64.3		
0.223	63	0.223	63.9	0.226	63.7		

(continued)

Detergent Control 1					
Samp	le A	Samp	le B	Sample C	
τ	γ	τ	γ	τ	γ
0.313	62.6	0.313	63.7	0.315	63.8
0.421	62.5	0.426	63.5	0.149	63.2
0.624	62.3	0.622	62.7	0.621	62.7
0.857	61.4	0.878	62.7	0.883	62.9
1.164	62	1.148	62.4	1.149	62.2
1.659	61.7	1.648	62.1	1.656	62.3
2.495	61.2	2.527	61.1	2.532	61.4
3.217	60.7	3.145	60.9	3.185	61.3
4.388	59.7	4.28	60.3	4.162	60.6
6.463	57.6	6.62	57.3	6.166	59.2
8.781	54.7	9.156	53.7	8.342	55.5
11.244	52	13.403	52.1	11.972	52.7
18.795	45.7	15.816	45.7	16.933	51
21.721	44.4	21.895	47.7	22.163	47.4

TABLE 4B

Detergent Control 2						
Samp	le A	Samp	Sample B		Sample C	
τ	Γ	τ	γ	τ	γ	
0.031	65.8	0.03	66.6	0.03	65.8	
0.041	65.9	0.041	66	0.042	65.6	
0.058	65.5	0.058	65.1	0.058	64.6	
0.082	64.7	0.082	64.7	0.082	64.1	
0.115	63.9	0.115	63.9	0.116	63.8	
0.161	64	0.162	63.6	0.16	63.5	
0.226	63.5	0.223	62.9	0.225	63.2	
0.317	63.6	0.316	62.4	0.315	63	
0.429	63.3	0.428	61.9	0.42	62.4	
0.629	62.2	0.623	61	0.632	61.7	
0.888	61.7	0.882	59.7	0.867	60.9	
1.171	61.5	1.145	59.2	1.114	60.4	
1.673	60.5	1.57	58.2	1.607	59.5	
2.515	58.8	2.451	55.1	2.409	58.4	
2.993	57.4	2.878	54	2.945	57	
4.326	54.8	4.113	51.5	4.015	55.6	

(continued)

	Detergent Control 2						
	Samp	le A	Sample B		Sample C		
	τ	Γ	τ	γ	τ	γ	
	6.455	52.6	5.751	49.9	6.017	53.2	
	8.989	49.9	9.861	46.7	7.906	50.4	
1	11.373	44.3	12.865	44.1	12.578	46.6	
1	16.815	43.1	15.861	43.8	17.397	45	
	23.12	40.9	22.161	41.5	26.01	44.7	

TABLE 4C

TABLE 4C							
Rinse Aid Control 1							
Samp	le A	Samp	le B	Samp	le C		
τ	Γ	τ	γ	τ	γ		
0.031	66.3	0.03	65.6	0.03	65.6		
0.042	66.2	0.041	65.6	0.042	65.6		
0.058	65.1	0.058	64.8	0.058	64.8		
0.082	64.8	0.081	63.9	0.081	63.9		
0.114	65.1	0.115	63.6	0.113	63.4		
0.161	64.3	0.16	63.5	0.159	63.1		
0.227	63.8	0.227	62.7	0.225	62.7		
0.317	63.1	0.317	62.5	0.313	62.3		
0.44	62.4	0.426	61.9	0.425	61.8		
0.619	61.5	0.626	61.4	0.622	60.8		
0.848	59.8	0.866	60	0.879	59.7		
1.173	58.8	1.152	59	1.143	58.8		
1.641	56.7	1.601	57.5	1.592	57.5		
2.491	54.8	2.381	55.3	2.336	55.3		
3.126	53.9	2.862	54.6	2.979	54.4		
4.692	52.2	4.014	52.9	4.46	52.4		
6.112	51.7	5.869	51.5	6.398	50.9		
8.935	51	8.418	51	9.057	50.7		
11.571	51	12.22	49.9	12.613	49.9		
18.684	49.9	18.629	49.9	17.07	49.1		
29.293	48.3	24.928	48.7	21.252	49		

TABLE 4D

	Rinse Aid Control 2						
Samp	le A	Sample B		Sample C			
τ	Γ	τ	γ	τ	γ		
0.031	65.6	0.03	66	0.03	66.1		
0.041	65.5	0.041	64.6	0.042	65.7		
0.058	64.5	0.058	64.5	0.057	63.8		
0.082	64.8	0.082	64.2	0.082	64		
0.113	64.2	0.113	63.1	0.116	63.7		
0.16	63.6	0.162	62.7	0.162	62.5		
0.225	62.9	0.228	61.9	0.22	61.5		
0.313	61.8	0.312	60	0.314	60.5		
0.424	60.2	0.417	58.6	0.424	58.7		
0.592	57.2	0.621	56.4	0.609	55.9		
0.856	55.4	0.874	54.3	0.854	53.9		
1.119	53.9	1.097	52.4	1.115	52		
1.612	52.4	1.609	50.5	1.539	50.6		
2.476	49.9	2.363	48.1	2.26	44.8		
3.115	48.2	2.835	47.7	2.831	43.9		
4.619	45.7	4.461	43.3	4.588	40.9		
7.16	41.8	5.675	41	5.839	39.4		
8.653	41.5	8.914	39.1	8.727	37.7		
11.358	40.7	11.159	38	12.111	35.3		
		15.255	36.4	15.955	34.8		
				21.85	33.1		

TABLE 4E

17.6522 12							
	Experimental Formulation (Exp1)						
Samp	le A	Samp	le B	Samp	le C		
τ	Γ	τ	γ	τ	γ		
0.03	65.5	0.031	65.4	0.03	64.8		
0.041	64.6	0.041	64.6	0.041	65.2		
0.057	63.8	0.058	64.5	0.058	63.8		
0.081	63.1	0.08	63.5	0.082	62.8		
0.113	61.7	0.116	62.7	0.115	61.5		
0.162	60.7	0.16	61.9	0.16	60.2		
0.221	59.2	0.226	60.4	0.222	59.2		
0.312	57.4	0.315	58.8	0.315	57.7		
0.423	56.2	0.42	57.2	0.419	56.3		
0.618	54	0.622	55.6	0.612	54.6		

(continued)

	Experimental Formulation (Exp1)										
Samp	le A	Samp	le B	Sample C							
τ	Γ	τ	γ	τ	γ						
0.888	52.4	0.883	54.1	0.846	53.1						
1.147	51.2	1.151	52.8	1.166	52						
1.701	50.3	1.628	51.6	1.712	50.9						
2.56	48.9	2.54	50.1	2.329	49.6						
3.123	48.5	3.047	49.4	2.973	48.6						
4.063	46.8	4.343	48.3	4.017	47.3						
7.141	44.7	6.97	46.2	5.615	45.7						
9.383	43	10.408	43.1	8.816	43.9						
12.358	41.6	12.122	44.3	11.387	42.5						
19.243	29.5	19.097	42	15.941	41.2						
21.458	38.4	21.608	40.7	23.455	39.5						

TABLE 4F

DI						
Sampl	le A					
τ	γ					
0.031	66.5					
0.041	65					
0.058	65.5					
0.082	64.7					
0.115	65.3					
0.159	64.6					
0.226	64.7					
0.308	64.8					
0.424	64.5					
0.613	64.7					
0.876	64.2					
1.168	64.5					
1.711	64.2					
2.647	64.3					
3.191	64.5					
4.628	63.8					
6.705	64.1					
10.707	64					

[0131] The average surface tension at 160 °F for the average bubble life times of 0.3, 1.6, 3.0, and 9.1 seconds was

tested. The results are provided in Table 5.

#### TABLE5

Sample	Avg. Surface Tension at 0.3 s	Avg. Surface Tension at 1.6 s	Avg. Surface Tension at 3.0 s	Avg. Surface Tension at 9.1 s
DI water	64.8	64.2	64.5	64.0
Detergent Control 1	63.0	59.4	56.1	49.0
Detergent Control 2	63.4	62.0	61.0	54.6
Rinse Aid Control 1	62.6	57.2	54.3	50.9
Rinse Aid Control 2	60.8	51.2	46.6	39.2
Exp. 1	58.0	50.9	48.8	43.3

**[0132]** The data demonstrates the surface tension of Experimental Formulation 1 decreases quickly with a significant drop in surface tension at the bubble life time of 9.1 seconds. This is similar to a well-performing rinse aid, such as Rinse Aid Control 2. These results are demonstrated in Figure 1.

## **EXAMPLE 2**

5

10

15

20

25

35

45

50

55

#### ONE HUNDRED-CYCLE FILM EVALUATION FOR INSTITUTIONAL WAREWASH DETERGENTS

[0133] To determine the ability of various detergent compositions to remove spots and film from ware, six Libby 10 oz. glass tumblers were prepared by removing all film and foreign material from the surfaces of the glasses. A Hobart AM-15 warewash machine was then filled with an appropriate amount of water and the water was tested for hardness. After recording the hardness value, the tank heaters were turned on. On the day of the experiments, the water hardness was 17 grains. The warewash machine was turned on and wash/rinse cycles were run through the machine until a wash temperature of between about 150°F and about 160°F and a rinse temperature of between about 175°F and about 190°F were reached. The controller was then set to dispense an appropriate amount of detergent into the wash tank. The detergent was dispensed such that when the detergent was mixed with water during the cycle to form a use solution, the detergent concentration in the use solution was 750 parts per million (ppm). The solution in the wash tank was titrated to verify detergent concentration. The warewash machine had a washbath volume of 58 liters, a rinse volume of 2.8 liters, a wash time of 50 seconds, and a rinse time of 9 seconds.

**[0134]** The six clean glass tumblers were placed diagonally in a Raburn rack and four Newport 10 oz. plastic tumblers were placed off-diagonally in the Raburn rack (see figure below for arrangement) and the rack was placed inside the warewash machine. (P=plastic tumbler; G=glass tumbler).

					G
				G	
			G		
		G			
	G			Р	
G					

**[0135]** The 100 cycle test was then started. At the beginning of each wash cycle, the appropriate amount of detergent was automatically dispensed into the warewash machine to maintain the initial detergent concentration. The detergent concentration was controlled by conductivity.

**[0136]** Upon completion of 100 cycles, the rack was removed from the warewash machine and the glass and plastic tumblers were allowed to dry. The glass and plastic tumblers were then graded for spot and film accumulation using film

ratings and using an analytical light box evaluation. The film rating scale is provided in Table 6.

5

10

15

20

25

30

35

40

45

50

55

#### TABLE 6

Rating	Spots	Film
1	No spots	No Film
2	Spots at random	20% of surface covered in film
3	1/4 glass spotted	40% of the surface covered in film
4	1/2 glass spotted	60% of the surface covered in film
5	Whole glass spotted	At least 80% of the surface covered in film

**[0137]** The light box test used a digital camera, a light box, a light source, a light meter and a control computer employing "Spot Advance" and "Image Pro Plus" commercial software. A glass to be evaluated was placed on its side on the light box, and the intensity of the light source was adjusted to a predetermined value using the light meter. A photographic image of the glass was taken and saved to the computer. The software was then used to analyze the upper half of the glass, and the computer displayed a histogram graph with the area under the graph being proportional to the thickness of the film.

**[0138]** Generally, a lower light box score indicates that more light was able to pass through the tumbler. Thus, the lower the light box score, the more effective the composition was at preventing scale on the surface of the tumbler. A clean, unused glass tumbler has a light box score of approximately 12,000, which corresponds to a score of 72,000 for the six glass tumblers, and a clean, unused plastic tumbler has a light box score of approximately 25,500, which corresponds to a light box score of approximately 102,000 for the four plastic tumblers. The minimum obtainable light box score (i.e., sum of six clean glass tumblers and four clean plastic tumblers) is approximately 174,000. Generally, a detergent composition is considered effective for controlling hard water scale if the sum of the light box scores for six glass tumblers and four plastic tumblers is approximately 360,000 or less.

**[0139]** The results of the 100-Cycle test are provided in Tables 7-8 providing average film ratings for glasses and plastic tumbler.

TABLE 7

100-cycle Film							Avg. Glass Score (St. Dev.)	Plastic Score
	G1	G2	G3	G4	G5	G6		P1
Detergent Control 1	4.5	3.0	3.5	4.5	3.5	4.0	3.8 (0.6)	1.5
Detergent Control 2	5.0	3.5	4.0	4.5	4.5	4.0	4.3 (0.5)	2.5
Detergent Control 1 + Rinse Aid Control 2	4.5	4.0	4.5	4.5	4.0	5.0	4.4 (0.3)	3.5
Detergent Control 2 + Rinse Aid Control 1	4.5	3.0	4.0	4.0	3.5	4.0	3.8 (0.5)	2.5
Exp. 1	2.0	2.0	2.0	2.0	2.0	2.5	2.1 (0.2)	2.0

TABLE 8

100-cycle Light box							Summe d Glass Score	Plastic Score	Summe d Total Score
	G1	G2	G3	G4	G5	G6		P1	
Detergent Control 1	Maxed (65535)	38906	55734	62998	47238	59893	330304	17681	347985
Detergent Control 2	Maxed (65535)	55061	59141	63854	63879	59859	367329	31530	398859

(continued)

100-cycle Light box							Summe d Glass Score	Plastic Score	Summe d Total Score
	G1	G2	G3	G4	G5	G6		P1	
Detergent Control 1 + Rinse Aid Control 2	Maxed (65535)	63291	65304	65226	65412	Maxed (65535)	390303	46448	436751
Detergent Control 2 + Rinse Aid	Maxed (65535)	42699	54556	56364	50826	59589	329589	30727	360296
Control 1									
Exp. 1	22329	19107	19692	19122	20387	22797	123434	23554	146988

## EXAMPLE 3

#### FIFTY CYCLE REDEPOSITION EXPERIMENT FOR INSTITUTIONAL WAREWASH DETERGENTS

**[0140]** The cleaning efficacy of the compositions according to the invention and controls were further evaluated using a 50 cycle redeposition experiment for institutional ware wash detergents. To test the ability of compositions to clean glass and plastic, 6 10 oz. Libby heat resistant glass tumblers and 1 plastic tumblers were used. The glass tumblers were cleaned prior to use. New plastic tumblers were used for each experiment.

**[0141]** A food soil solution was prepared using a 50/50 combination of beef stew and hot point soil and employed at 2000 ppm soil. The soil included two cans of Dinty Moore Beef Stew (1360 grams), one large can of tomato sauce (822 grams), 15.5 sticks of Blue Bonnet Margarine (1746 grams) and powered milk (436.4 grams). The hot point soil was added to the machine to maintain a sump concentration of about 2000 ppm.

**[0142]** After filling the dishmachine with 17 grain water, the heaters were turned on. The wash temperature was adjusted to about 150-160°F. The final rinse temperature was adjusted to about 175-190°F. The controller was set to disclose the amount of detergent in the wash tank. The glass and plastic tumblers were placed in the Raburn rack (see figure below for arrangement; P=plastic tumbler; G=glass tumbler) and the rack was placed inside the dishmachine.

					G6
				G5	
			G4		
		G3			
	G2			Р	
G1					

**[0143]** The dishmachine was then started and run through an automatic cycle. At the beginning of each cycle the appropriate amount of hot point sol was added to maintain the sump concentration of 2000 ppm. The detergent concentration is controlled by conductivity.

[0144] When the 50 cycles ended, the glasses were allowed to dry overnight. Thereafter they were graded for spots and film accumulation (visual).

**[0145]** The glass and plastic tumblers were then graded for protein accumulation using Commassie Brilliant Blue R stain followed by destaining with an aqueous acetic acid/methanol solution. The Commassie Brilliant Blue R stain was prepared by combining 1.25 g of Commassie Brilliant Blue R dye with 45 mL of acetic acid and 455 mL of 50% methanol in distilled water. The destaining solution consisted of 45% methanol and 10% acetic acid in distilled water.

**[0146]** The amount of protein remaining on the glass and plastic tumblers after destaining was rated visually on a scale of 1 to 5. A rating of 1 indicated no protein was present after destaining - no spots/no film. A rating of 2 indicated that random areas (barely perceptible) were covered with protein after destaining - spots at random (or about 20%).

28

5

15

10

20

25

35

45

40

50

surface covered in film). A rating of 3 indicated that about a quarter to half of the surface was covered with protein after destaining (or about 40% surface covered in film). A rating of 4 indicated that about half of the glass/plastic surface was covered with protein after destaining (or about 60% surface covered in film). A rating of 5 indicated that the entire surface was coated with protein after destaining (or at least about 80% surface covered in film).

**[0147]** The ratings of the glass tumblers tested for soil removal were averaged to determine an average soil removal rating from glass surfaces and the ratings of the plastic tumblers tested for soil removal were averaged to determine an average soil removal rating from plastic surfaces. Similarly, the ratings of the glass tumblers tested for redeposition were averaged to determine an average redeposition rating for glass surfaces and the ratings of the plastic tumblers tested for redeposition were averaged to determine an average redeposition rating for plastic surfaces.

**[0148]** The results are shown in following tables, demonstrating that the detergent compositions according to the invention provide at least substantially similar cleaning efficacy and in various embodiments provide superior efficacy over commercial products. The rating scale is shown in Table 9.

TABLE 9

Rating Spots Film No Film 1 No spots 2 Spots at random 20% of surface covered in film 3 40% of the surface covered in film 1/4 glass spotted 4 1/2 glass spotted 60% of the surface covered in film 5 Whole glass spotted At least 80% of the surface covered in film

[0149] The results of the 50-Cycle test are provided in Tables 10-11.

10

15

20

25

30

35

40

45

50

55

TABLE 10

50-cycle Spots							Avg. Glass Score (St. Dev.)	Plastic Score
	G1	G2	G3	G4	G5	G6		P1
Detergent Control 1	1.5	1.5	1.0	1.5	1.0	1.0	1.3 (0.3)	4.0
Detergent Control 2	2.0	1.5	1.5	1.0	2.0	1.5	1.6 (0.3)	1.5
Detergent Control 1 + Rinse Aid Control 2	1.5	1.5	1.0	1.0	1.5	1.5	1.3 (0.3)	5.0
Detergent Control 2 + Rinse Aid Control 1	1.5	1.0	1.0	1.0	1.0	1.5	1.2 (0.2)	1.0
Exp. 1	1.5	1.0	1.0	1.0	1.0	1.0	1.1 (0.2)	5.0

TABLE 11

50-cycle Film							Avg. Glass Score (St. Dev.)	Plastic Score
	G1	G2	G3	G4	G5	G6		P1
Detergent Control 1	2.0	3.0	2.0	2.0	3.0	4.5	2.8 (1.0)	1.5
Detergent Control 2	5.0	4.5	4.5	5.0	4.5	5.0	4.8 (0.3)	3.0
Detergent Control 1 + Rinse Aid Control 2	5.0	2.0	2.0	3.0	2.5	4.5	3.2 (1.3)	3.0
Detergent Control 2 + Rinse Aid Control 1	5.0	4.5	5.0	5.0	4.5	5.0	4.9 (0.3)	3.0
Exp. 1	5.0	3.0	4.0	4.5	3.5	5.0	4.2 (0.7)	1.0

### **EXAMPLE 4**

5

10

15

20

25

30

7-CYCLE SPOT, FILM & SOIL REMOVAL EVALUATION FOR INSTITUTIONAL WAREWASH DETERGENTS OR RINSE AIDS

**[0150]** To test the ability of compositions to clean glass and plastic, twelve 10 oz. Libbey heat resistant glass tumblers and four Newport plastic tumblers were used. The glass tumblers were cleaned prior to use.

**[0151]** A food soil solution was prepared using a 50/50 combination of beef stew and hot point soil. The concentration of the solution was about 2000 ppm. The soil included two cans of Dinty Moore Beef Stew (1360 grams), one large can of tomato sauce (822 grams), 15.5 sticks of Blue Bonnet Margarine (1746 grams) and powered milk (436.4 grams).

**[0152]** The dishmachine was then filled with an appropriate amount of water. After filling the dishmachine with the water, the heaters were turned on. The final rinse temperature was adjusted to about 180.degree. F. The glasses and plastic tumblers were soiled by rolling the glasses in a 1:1 (by volume) mixture of Campbell's Cream of Chicken Soup: Kemp's Whole Milk three times. The glasses were then placed in an oven at about 160.degree. F. for about 8 minutes. While the glasses were drying, the dishmachine was primed with about 120 grams of the food soil solution, which corresponds to about 2000 ppm of food soil in the pump.

**[0153]** The soiled glass and plastic tumblers were placed in the Raburn rack (see figure below for arrangement; P=plastic tumbler; G=glass tumbler) and the rack was placed inside the dishmachine. The first two columns with the tumblers were tested for soil removal while the second two columns with the tumblers were tested for redeposition.

Soil Redeposition Removal

35

40

45

50

55

**[0154]** The dishmachine was then started and run through an automatic cycle. When the cycle ended, the top of the glass and plastic tumblers were mopped with a dry towel. The glass and plastic tumblers being tested for soil removal were removed and the soup/milk soiling procedure was repeated. The redeposition glass and plastic tumblers were not removed.

**[0155]** At the beginning of each cycle, an appropriate amount of detergent and food soil were added to the wash tank to make up for the rinse dilution. The soiling and washing steps were repeated for seven cycles.

**[0156]** The glass and plastic tumblers were then graded for protein accumulation using Coommassie Brilliant Blue R stain followed by destaining with an aqueous acetic acid/methanol solution. The Coommassie Brilliant Blue R stain was prepared by combining about 1.25 g of Coommassie Brilliant Blue R dye with about 45 mL of acetic acid and about 455 mL of 50% methanol in distilled water. The destaining solution consisted of 45% methanol and 10% acetic acid in distilled water. The amount of protein remaining on the glass and plastic tumblers after destaining was rated visually on a scale of 1 to 5. A rating of 1 indicated no protein was present after destaining. A rating of 2 indicated that random areas (barely perceptible) were covered with protein after destaining. A rating of 3 indicated that about a quarter of the surface was covered with protein after destaining. A rating of 5 indicated that the entire surface was coated with protein after destaining.

**[0157]** The ratings of the glass tumblers tested for protein removal were averaged to determine an average protein removal rating from glass surfaces and the ratings of the plastic tumblers tested for protein removal were averaged to determine an average protein removal rating from plastic surfaces. Similarly, the ratings of the glass tumblers tested for redeposition were averaged to determine an average protein redeposition rating for glass surfaces and the ratings of the plastic tumblers tested for protein redeposition were averaged to determine an average protein redeposition rating for plastic surfaces.

**[0158]** Glasses are rated visually in the glass viewing area against a black background. Rate each set of glasses as a set, i.e., all redeposition glasses for all products tested. An overall average can be determined for each set. The rating

scale used is shown in Table 12.

TABLE 12

Rating	Spots	Film	Protein
1	No spots	No Film	No Protein
2	Spots at random	20% of surface covered in film	20% remains
3	1/4 glass spotted	40% of the surface covered in film	40% remains
4	1/2 glass spotted	60% of the surface covered in film	80% remains
5	Whole glass spotted	At least 80% of the surface covered in film	100% remains

**[0159]** The results of the 7-Cycle test are provided in Tables 13-14 showing average spotting, film, and protein staining ratings (with standard deviation) for glasses and plastic tumblers:

TABLE 13

7-cycle Redeposition	Exp.	Detergent Control 1	Detergent Control 2	Detergent Control 1+ Rinse Aid Control 2	Detergent Control 2+ Rinse Aid Control 1	Exp. 1
Avg. Glass Score Spots	1	5.0 (0.0)	5.0 (0.0)	1.0 (0.0)	5.0 (0.0)	2.3 (0.6)
	2					3.9 (1.5)
	3					1.9 (1.0)
Avg. Glass Score Film	1	1.0 (0.0)	1.2 (0.2)	1.77 (0.2)	1.0 (0.0)	3.6 (0.4)
	2					2.1 (1.5)
	3					4.0 (1.0)
Avg. Protein Glass Score	1	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)
	2					1.0 (0.0)
	3					1.0 (0.0)
Avg. Protein Plastic Score	1	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)
	2					1.5 (0.5)
	3					1.0 (0.0)

### TABLE 14

	7-cycle Soil removal	Ехр.	Detergent Control 1	Detergent Control 2	Detergent Control 1 + Rinse Aid Control 2	Detergent Control 2 + Rinse Aid Control 1	Exp. 1
5	Avg. Glass Score Spots	1	5.0 (0.0)	4.8 (0.2)	1.0 (0.0)	4.2 (1.1)	3.5 (1.2)
10		2					4.1 (0.9)
70		3					1.5 (0.7)
15	Avg. Glass Score Film	1	1.1 (0.2)	4.4 (0.2)	4.1 (0.9)	4.8 (0.2)	2.8 (1.2)
15		2					2.7 (1.0)
		3					4.3 (1.1)
20	Avg. Protein Glass Score	1	1.3 (0.3)	5.0 (0.0)	1.3 (0.3)	5.0 (0.0)	3.0 (1.0)
25		2					1.0 (0.0)
		3					1.0 (0.0)
30	Avg. Protein Plastic Score	1	1.0 (0.0)	5.0 (0.0)	1.0 (0.0)	5.0 (0.0)	1.8 (0.3)
35		2					1.0 (0.0)
55		3					1.5 (0.0)

## **EXAMPLES 5-8**

40

45

50

55

**[0160]** The materials used in the Examples 5-8 are provided herein:

Pluronic® 25R2: an EO/PO copolymer available from BASF.

Novel® II 1012GB-21: an alcohol alkoxylate available from Sasol.

Acusol® 448: a polyacrylic acid copolymer, available from the Dow Chemical Company.

[0161] Additional materials commercially-available from multiple sources include: sodium carbonate, ash monohydrate, sodium tripolyphosphate (anhydrous), zinc chloride, HEDP, and KOH.

[0162] An exemplary 2-in-1 detergent comprising a polymer was prepared and is shown in Table 15. Throughout Examples, the formulation is referred to as Experimental Formula 2 (Exp. 2).

TABLE 15

Raw material	Exp. 2
Alkalinity source	45-75
Builder	10-30

(continued)

Raw material	Exp. 2
EO/PO copolymer	1-20
Alcohol alkoxylate	1-10
Polycarboxylic acid polymer	1-10
Corrosion inhibitor	0.01-0.5
Phosphonate builder, 60%	1-10
KOH, 45%	1-10
Total	100

[0163] Existing detergents, rinse aids, and Experimental Formula 2 were tested against distilled water. Detergent Control 1 and Detergent Control 2 are commercially available detergents (phosphate-based detergents). Rinse Aid Control 1 and rinse Aid Control are two commercially available rinse aids (employing higher amounts of active ingredients surfactants of at least two ionic categories (e.g., nonionic and cationic)). The use concentrations for all experiments described below are provided in Table 16:

TABLE 16

Sample	Use concentration [ppm]
DI water	N/A
Detergent Control 1	1500
Detergent Control 2	1000
Rinse Aid Control 1	536
Rinse Aid Control 2	536
Exp. 2	1415

[0164] All warewash testing was performed with 10 oz. Libbey glasses on a Hobart AM-15 warewash machine. The specifications of the Hobart AM-15 warewash machine are as follows:

Hobart AM-15 warewash machine specifications.

Washbath volume:	53L
Rinse volume:	2.8L
Wash time:	50 sec.
Rinse time:	9 sec.

## 45 EXAMPLE 5

5

10

25

30

40

50

55

## DYNAMIC SURFACE TENSION

**[0165]** The SITA science line t60 measures the dynamic surface tension of liquids up to the semi-static range. Air bubbles are generated from a capillary with known radius. The bubble pressure is measured as a function of bubble life time, which can be correlated to the surface tension according to the Young-Laplace equation. Dynamic surface tension provides insight into the dynamic behavior of surfactants and other surface active compounds under dynamic conditions, i.e. how quick surfactants can reach a surface. The dynamic surface tension is a function of concentration, temperature and type of surfactant. The dynamic surface tension behavior of surfactants is particularly important in applications where a quick response of surfactants is required, for example, in the short rinse cycles of automated dishwashing.

#### APPARATUS AND MATERIALS:

### [0166]

5

10

15

- 1. SITA T60 (Sita Messtechnik, Germany)
- 2. Oil bath with stir bar
- 3. Heating and stirring plate
- 4. Glass beakers
- 5. Glass vials (20 mL)

[0167] The SITA science line t60 was calibrated with DI water. Clean water samples after calibration should have a surface tension of  $72.0\pm1.0$ mN/m (depending on water quality and temperature). Following calibration, the SITA was programmed to take readings at the desired time intervals (i.e., 0.3, 1.6, 3.0, and 9.1 seconds). Three separate solutions at the desired ppm were prepared for each composition (described as A-C) to be tested (e.g., three samples of Exp. 2, three samples of Detergent Control 1). 10-15 mL were transferred into 20 mL vials and immersed in a heated oil bath to 72 °C (160 °F)  $\pm$  2°C. The samples were equilibrated for 10-15 minutes. The samples were individually removed from the oil bath and the tested in the SITA. After each sample was tested the SITA's cleaning procedure was run, then the surface tension of DI water was checked to ensure the SITA was adequately clean. If the DI water measurements were not within  $72.0 \pm 1.0$  mN/m, then the cleaning procedure was run again. The surface tension (mN/m) versus bubble life time at 160 °F experimental data is provided in Tables 17-A through 17-F below, where  $\tau$  is the bubble life time in seconds and  $\gamma$  is the surface tension in mN/m.

TABLE 17-A

25		
30		
35		
40		
45		
50		

Detergent Control 1							
Samp	le A	Samp	le B	Sample C			
τ	γ	τ	γ	τ	γ		
0.031	65.1	0.031	67.9	0.03	66.4		
0.041	65	0.042	65.9	0.041	66.2		
0.058	64.5	0.058	65.8	0.058	65		
0.083	64.1	0.082	65.3	0.081	64.1		
0.116	63.4	0.116	64.6	0.116	64.4		
0.159	62.8	0.161	63.8	0.162	64.3		
0.223	63	0.223	63.9	0.226	63.7		
0.313	62.6	0.313	63.7	0.315	63.8		
0.421	62.5	0.426	63.5	0.419	63.2		
0.624	62.3	0.622	62.7	0.621	62.7		
0.857	61.4	0.878	62.7	0.883	62.9		
1.164	62	1.148	62.4	1.149	62.2		
1.659	61.7	1.648	62.1	1.656	62.3		
2.495	61.2	2.527	61.1	2.532	61.4		
3.217	60.7	3.145	60.9	3.185	61.3		
4.388	59.7	4.28	60.3	4.162	60.6		
6.463	57.6	6.62	57.3	6.166	59.2		
8.781	54.7	9.156	53.7	8.342	55.5		
11.244	52	13.403	52.1	11.972	52.7		
18.795	45.7	15.816	45.7	16.933	51		
21.721	44.4	21.895	47.7	22.163	47.4		

TABLE 17-B

Detergent Control 2							
$\gamma$	amp	Samp	npi	le B		Samp	le C
		τ		γ		τ	γ
3	.03	0.03	3	66.6	6	0.03	65.8
1	)41	041	1	66	6	0.042	65.6
8	)58	058	8	65.1		0.058	64.6
2	)82	082	2	64.7	,	0.082	64.1
5	115	115	5	63.9	)	0.116	63.8
2	162	162	2	63.6	6	0.16	63.5
3	223	223	3	62.9	)	0.225	63.2
6	316	316	6	62.4	Ļ	0.315	63
8	128	428	8	61.9	)	0.42	62.4
3	523	623	3	61		0.632	61.7
2	382	882	2	59.7	,	0.867	60.9
5	145	145	5	59.2	)	1.114	60.4
7	.57	1.57	7	58.2	2	1.607	59.5
1	151	451	1	55.1		2.409	58.4
8	378	878	8	54		2.945	57
3	113	113	3	51.5	5	4.015	55.6
1	751	751	1	49.9	)	6.017	53.2
1	361	861	1	46.7	,	7.906	50.4
5	365	865	5	44.1		12.578	46.6
1	361	861	1	43.8	}	17.397	45
1	161	161	1	41.5	5	26.01	44.7

TABLE 17-C

Rinse Aid Control 1								
Samp	le A	Samp	le B	Sample C				
τ	Γ	τ	γ	τ	γ			
0.031	66.3	0.03	65.6	0.03	65.6			
0.042	66.2	0.041	65.6	0.042	65.6			
0.058	65.1	0.058	64.8	0.058	64.8			
0.082	64.8	0.081	63.9	0.081	63.9			
0.114	65.1	0.115	63.6	0.113	63.4			
0.161	64.3	0.16	63.5	0.159	63.1			
0.227	63.8	0.227	62.7	0.225	62.7			
0.317	63.1	0.317	62.5	0.313	62.3			
0.44	62.4	0.426	61.9	0.425	61.8			

(continued)

Rinse Aid Control 1								
Samp	le A	Samp	le B	Sample C				
τ	Γ	τ	γ	τ	γ			
0.619	61.5	0.626	61.4	0.622	60.8			
0.848	59.8	0.866	60	0.879	59.7			
1.173	58.8	1.152	59	1.143	58.8			
1.641	56.7	1.601	57.5	1.592	57.5			
2.491	54.8	2.381	55.3	2.336	55.3			
3.126	53.9	2.862	54.6	2.979	54.4			
4.692	52.2	4.014	52.9	4.46	52.4			
6.112	51.7	5.869	51.5	6.398	50.9			
8.935	51	8.418	51	9.057	50.7			
11.571	51	12.22	49.9	12.613	49.9			
18.684	49.9	18.629	49.9	17.07	49.1			
29.293	48.3	24.928	48.7	21.252	49			

TABLE 17-D

Rinse Aid Control 2								
Sample A		Samp	le B	Sample C				
τ	Γ	τ	γ	τ	γ			
0.031	65.6	0.03	66	0.03	66.1			
0.041	65.5	0.041	64.6	0.042	65.7			
0.058	64.5	0.058	64.5	0.057	63.8			
0.082	64.8	0.082	64.2	0.082	64			
0.113	64.2	0.113	63.1	0.116	63.7			
0.16	63.6	0.162	62.7	0.162	62.5			
0.225	62.9	0.228	61.9	0.22	61.5			
0.313	61.8	0.312	60	0.314	60.5			
0.424	60.2	0.417	58.6	0.424	58.7			
0.592	57.2	0.621	56.4	0.609	55.9			
0.856	55.4	0.874	54.3	0.854	53.9			
1.119	53.9	1.097	52.4	1.115	52			
1.612	52.4	1.609	50.5	1.539	50.6			
2.476	49.9	2.363	48.1	2.26	44.8			
3.115	48.2	2.835	47.7	2.831	43.9			
4.619	45.7	4.461	43.3	4.588	40.9			
7.16	41.8	5.675	41	5.839	39.4			
8.653	41.5	8.914	39.1	8.727	37.7			

(continued)

	Rinse Aid Control 2											
Samp	le A	Samp	le B	Sample C								
τ	Γ	τ	γ	τ	γ							
11.358	40.7	11.159	38	12.111	35.3							
		15.255	36.4	15.955	34.8							
				21.85	33.1							

TABLE 17-E

	TABLE 17-E											
	Experimental Formulation (Exp.2)											
Sampl	le A	Samp	ole B	Sample C								
<u>τ</u>	$\underline{\Gamma}$	<u>τ</u>	Υ	<u>τ</u>	Υ							
0.03	64.7	0.03	66.7	0.031	65.6							
0.41	64.3	0.43	65.3	0.043	64.3							
0.058	66.1	0.058	64.4	0.058	63.2							
0.083	63.9	0.081	62.5	0.082	62.5							
0.118	62	0.116	61.5	0.116	60.6							
0.167	59.9	0.161	60.2	0.161	59.3							
0.221	58.5	0.225	58.8	0.225	57.8							
0.313	57.6	0.313	57.1	0.313	56.3							
0.427	57.6	0.43	525.6	0.423	55							
0.627	54.3	0.622	54.4	0.632	53.7							
0.871	54.4	0.867	53.3	0.886	52.7							
1.169	52.8	1.161	52.3	1.145	52.2							
1.727	536	1.652	51.5	1.656	51							
2.467	52.5	2.543	50.4	2.572	50.3							
3.145	52	3.515	49.9	3.092	50.2							
4.234	20.9	4.49	49.1	4.389	49.3							
6.126	50.3	6.261	48.3	6.106	48.4							
9.11	48.1	8.886	47.7	8.891	47.3							
12.609	48.2	11.701	46.7	12.448	46.5							
18.514	47.1	17.215	45.4	17.854	45.5							
22.164	45.3	23.579	44.9	23.081	44.7							

TABLE 17-F

DI								
Sample A								
τ	γ							
0.031	66.5							

(continued)

DI			
Samp	le A		
τ	γ		
0.041	65		
0.058	65.5		
0.082	64.7		
0.115	65.3		
0.159	64.6		
0.226	64.7		
0.308	64.8		
0.424	64.5		
0.613	64.7		
0.876	64.2		
1.168	64.5		
1.711	64.2		
2.647	64.3		
3.191	64.5		
4.628	63.8		
6.705	64.1		
10.707	64		

**[0168]** The average surface tension at 160  $^{\circ}$ F for the average bubble life times of 0.3, 1.6, 3.0, and 9.1 seconds was tested. The results are provided in Table 18.

TABLE 18

Sample	Avg. Surface Tension at 0.3 s	Avg. Surface Tension at 1.6 s	Avg. Surface Tension at 3.0 s	Avg. Surface Tension at 9.1 s
DI water	64.8	64.2	64.5	64.0
Detergent Control 1	63.0	59.4	56.1	49.0
Detergent Control 2	63.4	62.0	61.0	54.6
Rinse Aid Control 1	62.6	57.2	54.3	50.9
Rinse Aid Control 2	60.8	51.2	46.6	39.2
Exp. 2	57.0	52.0	50.7	47.7

**[0169]** The data demonstrates the surface tension of Experimental Formulation 2 decreases quickly with a significant drop in surface tension at the bubble life time of 9.1 seconds. This is similar to a well-performing rinse aid, such as Rinse Aid Control 2. These results are demonstrated in Figure 2.

### **EXAMPLE 6**

#### ONE HUNDRED-CYCLE FILM EVALUATION FOR INSTITUTIONAL WAREWASH DETERGENTS

[0170] To determine the ability of various detergent compositions to remove spots and film from ware, six Libby 10 oz. glass tumblers were prepared by removing all film and foreign material from the surfaces of the glasses. A Hobart AM-15 warewash machine was then filled with an appropriate amount of water and the water was tested for hardness. After recording the hardness value, the tank heaters were turned on. On the day of the experiments, the water hardness was 17 grains. The warewash machine was turned on and wash/rinse cycles were run through the machine until a wash temperature of between about 150°F and about 160°F and a rinse temperature of between about 175°F and about 190°F were reached. The controller was then set to dispense an appropriate amount of detergent into the wash tank. The detergent was dispensed such that when the detergent was mixed with water during the cycle to form a use solution, the detergent concentration in the use solution was 750 parts per million (ppm). The solution in the wash tank was titrated to verify detergent concentration. The warewash machine had a washbath volume of 58 liters, a rinse volume of 2.8 liters, a wash time of 50 seconds, and a rinse time of 9 seconds.

**[0171]** The six clean glass tumblers were placed diagonally in a Raburn rack and four Newport 10 oz. plastic tumblers were placed off-diagonally in the Raburn rack (see figure below for arrangement) and the rack was placed inside the warewash machine. (P=plastic tumbler; G=glass tumbler).

					G
				G	
			G		
		G			
	G			Р	
G					

[0172] The 100 cycle test was then started. At the beginning of each wash cycle, the appropriate amount of detergent was automatically dispensed into the warewash machine to maintain the initial detergent concentration. The detergent concentration was controlled by conductivity.

**[0173]** Upon completion of 100 cycles, the rack was removed from the warewash machine and the glass and plastic tumblers were allowed to dry. The glass and plastic tumblers were then graded for spot and film accumulation using film ratings and using an analytical light box evaluation. The film rating scale is provided in Table 19:

TABLE 19

Rating	Spots	Film
1	No spots	No Film
2	Spots at random	20% of surface covered in film
3	1/4 glass spotted	40% of the surface covered in film
4	1/2 glass spotted	60% of the surface covered in film
5	Whole glass spotted	At least 80% of the surface covered in film

**[0174]** The light box test used a digital camera, a light box, a light source, a light meter and a control computer employing "Spot Advance" and "Image Pro Plus" commercial software. A glass to be evaluated was placed on its side on the light box, and the intensity of the light source was adjusted to a predetermined value using the light meter. A photographic image of the glass was taken and saved to the computer. The software was then used to analyze the upper half of the glass, and the computer displayed a histogram graph with the area under the graph being proportional to the thickness of the film.

**[0175]** Generally, a lower light box score indicates that more light was able to pass through the tumbler. Thus, the lower the light box score, the more effective the composition was at preventing scale on the surface of the tumbler. A clean, unused glass tumbler has a light box score of approximately 12,000, which corresponds to a score of 72,000 for the six glass tumblers, and a clean, unused plastic tumbler has a light box score of approximately 25,500, which corre-

20

10

15

25

40

35

45

50

sponds to a light box score of approximately 102,000 for the four plastic tumblers. The minimum obtainable light box score (i.e., sum of six clean glass tumblers and four clean plastic tumblers) is approximately 174,000. Generally, a detergent composition is considered effective for controlling hard water scale if the sum of the light box scores for six glass tumblers and four plastic tumblers is approximately 360,000 or less.

[0176] The results of the 100-Cycle test are provided in Tables 20 and 21.

#### TABLE 20

100-cycle <u>Film</u>							Avg. Glass Score (St. Dev.)	Plastic Score
	G1	G2	G3	G4	G5	G6		P1
Detergent Control 1	4.5	3.0	3.5	4.5	3.5	4.0	3.8 (0.6)	1.5
Detergent Control 2	5.0	3.5	4.0	4.5	4.5	4.0	4.3 (0.5)	2.5
Detergent Control 1 + Rinse Aid Control 2	4.5	4.0	4.5	4.5	4.0	5.0	4.4 (0.3)	3.5
Detergent Control 2 + Rinse Aid Control 1	4.5	3.0	4.0	4.0	3.5	4.0	3.8 (0.5)	2.5
Exp. 2	3.0	1.5	1.5	1.5	1.5	2.0	1.8 (0.6)	2.0

## TABLE 21

25	100-cycle Light box							Summe d Glass Score	Plastic Score	Summed Total Score
		G1	G2	G3	G4	G5	G6		P1	
30	Detergent Control 1	Maxed (65535)	38906	55734	62998	47238	59893	330304	17681	347985
	Detergent Control 2	Maxed (65535)	55061	59141	63854	63879	59859	367329	31530	398859
35	Detergent Control 1 + Rinse Aid Control 2	Maxed (65535)	63291	65304	65226	65412	Maxed (65535)	390303	46448	436751
40	Detergent Control 2 + Rinse Aid Control 1	Maxed (65535)	42699	54556	56364	50826	59589	329589	30727	360296
	Exp. 2	34088	18832	18644	18790	19312	20966	130632	18685	149317

# EXAMPLE 7

45

50

5

10

15

20

### FIFTY CYCLE REDEPOSITION EXPERIMENT FOR INSTITUTIONAL WAREWASH DETERGENTS

- **[0177]** The cleaning efficacy of the compositions according to the invention and controls were further evaluated using a 50 cycle redeposition experiment for institutional ware wash detergents. To test the ability of compositions to clean glass and plastic, 6 10 oz. Libby heat resistant glass tumblers and 1 plastic tumblers were used. The glass tumblers were cleaned prior to use. New plastic tumblers were used for each experiment.
- [0178] A food soil solution was prepared using a 50/50 combination of beef stew and hot point soil and employed at 2000 ppm soil. The soil included two cans of Dinty Moore Beef Stew (1360 grams), one large can of tomato sauce (822 grams), 15.5 sticks of Blue Bonnet Margarine (1746 grams) and powered milk (436.4 grams). The hot point soil was added to the machine to maintain a sump concentration of about 2000 ppm.

**[0179]** After filling the dishmachine with 17 grain water, the heaters were turned on. The wash temperature was adjusted to about 150-160°F. The final rinse temperature was adjusted to about 175-190°F. The controller was set to disclose the amount of detergent in the wash tank. The glass and plastic tumblers were placed in the Raburn rack (see figure below for arrangement; P=plastic tumbler; G=glass tumbler) and the rack was placed inside the dishmachine.

					G6
				G5	
			G4		
		G3			
	G2			Р	
G1					

15

20

25

30

35

5

10

**[0180]** The dishmachine was then started and run through an automatic cycle. At the beginning of each cycle the appropriate amount of hot point sol was added to maintain the sump concentration of 2000 ppm. The detergent concentration is controlled by conductivity.

**[0181]** When the 50 cycles ended, the glasses were allowed to dry overnight. Thereafter they were graded for spots and film accumulation (visual).

**[0182]** The glass and plastic tumblers were then graded for protein accumulation using Commassie Brilliant Blue R stain followed by destaining with an aqueous acetic acid/methanol solution. The Commassie Brilliant Blue R stain was prepared by combining 1.25 g of Commassie Brilliant Blue R dye with 45 mL of acetic acid and 455 mL of 50% methanol in distilled water. The destaining solution consisted of 45% methanol and 10% acetic acid in distilled water.

**[0183]** The amount of protein remaining on the glass and plastic tumblers after destaining was rated visually on a scale of 1 to 5. A rating of 1 indicated no protein was present after destaining - no spots/no film. A rating of 2 indicated that random areas (barely perceptible) were covered with protein after destaining - spots at random (or about 20% surface covered in film). A rating of 3 indicated that about a quarter to half of the surface was covered with protein after destaining (or about 40% surface covered in film). A rating of 4 indicated that about half of the glass/plastic surface was covered with protein after destaining (or about 60% surface covered in film). A rating of 5 indicated that the entire surface was coated with protein after destaining (or at least about 80% surface covered in film).

**[0184]** The ratings of the glass tumblers tested for soil removal were averaged to determine an average soil removal rating from glass surfaces and the ratings of the plastic tumblers tested for soil removal were averaged to determine an average soil removal rating from plastic surfaces. Similarly, the ratings of the glass tumblers tested for redeposition were averaged to determine an average redeposition rating for glass surfaces and the ratings of the plastic tumblers tested for redeposition were averaged to determine an average redeposition rating for plastic surfaces.

**[0185]** The results are shown in following tables, demonstrating that the detergent compositions according to the invention provide at least substantially similar cleaning efficacy and in various embodiments provide superior efficacy over commercial products. The rating scale is shown in Table 22.

40

TABLE 22

45

Rating **Spots** Film No spots 1 No Film 2 Spots at random 20% of surface covered in film 3 1/4 glass spotted 40% of the surface covered in film 4 1/2 glass spotted 60% of the surface covered in film 5 Whole glass spotted At least 80% of the surface covered in film

50

[0186] The results of the 50-Cycle test are provided in Tables 23 and 24:

#### TABLE 23.

50-cycle Redeposition Spots							Avg. Glass Score (St. Dev.)	Plastic Score
	G1	G2	G3	G4	G5	G6		P1
Detergent Control 1	1.5	1.5	1.0	1.5	1.0	1.0	1.3 (0.3)	4.0
Detergent Control 2	2.0	1.5	1.5	1.0	2.0	1.5	1.6 (0.3)	1.5
Detergent Control 1 + Rinse Aid Control 2	1.5	1.5	1.0	1.0	1.5	1.5	1.3 (0.3)	5.0
Detergent Control 2 + Rinse Aid Control 1	1.5	1.0	1.0	1.0	1.0	1.5	1.2 (0.2)	1.0
Exp. 2	1.5	2.0	1.5	1.0	1.5	1.5	1.5 (0.3)	5.0

TABLE 24.

50-cycle Redeposition Film							Avg. Glass Score (St. Dev.)	Plastic Score
	G1	G2	G3	G4	G5	G6		P1
Detergent Control 1	2.0	3.0	2.0	2.0	3.0	4.5	2.8 (1.0)	1.5
Detergent Control 2	5.0	4.5	4.5	5.0	4.5	5.0	4.8 (0.3)	3.0
Detergent Control 1 + Rinse Aid Control 2	5.0	2.0	2.0	3.0	2.5	4.5	3.2 (1.3)	3.0
Detergent Control 2 + Rinse Aid Control 1	5.0	4.5	5.0	5.0	4.5	5.0	4.9 (0.3)	3.0
Exp. 2	4.0	3.5	3.5	4.0	4.0	4.5	3.9 (0.3)	1.0

## **EXAMPLE 8**

5

10

15

20

25

30

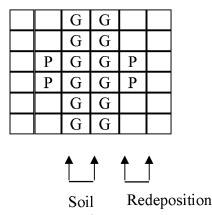
7-CYCLE SPOT, FILM & SOIL REMOVAL EVALUATION FOR INSTITUTIONAL WAREWASH DETERGENTS OR RINSE AIDS

**[0187]** To test the ability of compositions to clean glass and plastic, twelve 10 oz. Libbey heat resistant glass tumblers and four Newport plastic tumblers were used. The glass tumblers were cleaned prior to use.

**[0188]** A food soil solution was prepared using a 50/50 combination of beef stew and hot point soil. The concentration of the solution was about 2000 ppm. The soil included two cans of Dinty Moore Beef Stew (1360 grams), one large can of tomato sauce (822 grams), 15.5 sticks of Blue Bonnet Margarine (1746 grams) and powered milk (436.4 grams).

**[0189]** The dishmachine was then filled with an appropriate amount of water. After filling the dishmachine with the water, the heaters were turned on. The final rinse temperature was adjusted to about 180.degree. F. The glasses and plastic tumblers were soiled by rolling the glasses in a 1:1 (by volume) mixture of Campbell's Cream of Chicken Soup: Kemp's Whole Milk three times. The glasses were then placed in an oven at about 160.degree. F. for about 8 minutes. While the glasses were drying, the dishmachine was primed with about 120 grams of the food soil solution, which corresponds to about 2000 ppm of food soil in the pump.

[0190] The soiled glass and plastic tumblers were placed in the Raburn rack (see figure below for arrangement;
P=plastic tumbler; G=glass tumbler) and the rack was placed inside the dishmachine. The first two columns with the tumblers were tested for soil removal while the second two columns with the tumblers were tested for redeposition.



15 Removal

**[0191]** The dishmachine was then started and run through an automatic cycle. When the cycle ended, the top of the glass and plastic tumblers were mopped with a dry towel. The glass and plastic tumblers being tested for soil removal were removed and the soup/milk soiling procedure was repeated. The redeposition glass and plastic tumblers were not removed.

**[0192]** At the beginning of each cycle, an appropriate amount of detergent and food soil were added to the wash tank to make up for the rinse dilution. The soiling and washing steps were repeated for seven cycles.

[0193] The glass and plastic tumblers were then graded for protein accumulation using Coommassie Brilliant Blue R stain followed by destaining with an aqueous acetic acid/methanol solution. The Coommassie Brilliant Blue R stain was prepared by combining about 1.25 g of Coommassie Brilliant Blue R dye with about 45 mL of acetic acid and about 455 mL of 50% methanol in distilled water. The destaining solution consisted of 45% methanol and 10% acetic acid in distilled water. The amount of protein remaining on the glass and plastic tumblers after destaining was rated visually on a scale of 1 to 5. A rating of 1 indicated no protein was present after destaining. A rating of 2 indicated that random areas (barely perceptible) were covered with protein after destaining. A rating of 3 indicated that about a quarter of the surface was covered with protein after destaining. A rating of 4 indicated that about half of the glass/plastic surface was covered with protein after destaining. A rating of 5 indicated that the entire surface was coated with protein after destaining.

**[0194]** The ratings of the glass tumblers tested for protein removal were averaged to determine an average protein removal rating from glass surfaces and the ratings of the plastic tumblers tested for protein removal were averaged to determine an average protein removal rating from plastic surfaces. Similarly, the ratings of the glass tumblers tested for redeposition were averaged to determine an average protein redeposition rating for glass surfaces and the ratings of the plastic tumblers tested for protein redeposition were averaged to determine an average protein redeposition rating for plastic surfaces.

### **EVALUATION RESULTS:**

**[0195]** Glasses are rated visually in the glass viewing area against a black background. Rate each set of glasses as a set, i.e., all redeposition glasses for all products tested. An overall average can be determined for each set. The rating scale used is shown in Table 25.

TABLE 25

Rating	Spots	Spots Film			
1	No spots	No Film	No Protein		
2	Spots at random	20% of surface covered in film	20% remains		
3	1/4 glass spotted	40% of the surface covered in film	40% remains		
4	1/2 glass spotted	60% of the surface covered in film	80% remains		
5	Whole glass spotted	At least 80% of the surface covered in film	100% remains		

55

5

10

20

25

30

35

40

45

50

**[0196]** The results of the 7-Cycle test are provided in Tables 26 and 27 showing average spotting, film, and protein staining ratings (with standard deviation) for glasses and plastic tumblers.

# TABLE 26.

7-cycle Redeposition	Exp.	Detergent Control 1	Detergent Control 2	Detergent Control 1 + Rinse Aid Control 2	Detergent Control 2+ Rinse Aid Control 1	Exp. 2
Avg. Glass Score Spots	1	5.0 (0.0)	5.0 (0.0)	1.0 (0.0)	5.0 (0.0)	3.5 (1.4)
	2					2.3 (0.4)
	3					5.0 (0.0)
Avg. Glass Score Film	1	1.0 (0.0)	1.2 (0.2)	1.77 (0.2)	1.0 (0.0)	2.9 (1.1)
	2					2.6 (0.5)
	3					1.0 (0.0)
Avg. Protein Glass Score	1	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)
	2					1.0 (0.0)
	3					1.0 (0.0)
Avg. Protein Plastic Score	1	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)	1.0 (0.0)
	2					1.0 (0.0)
	3					1.0 (0.0)

TABLE 27.

7-cycle Soil removal	Ехр.	Detergent Control 1	Detergent Control 2	Detergent Control 1 + Rinse Aid Control 2	Detergent Control 2 + Rinse Aid Control 1	Exp. 2
Avg. Glass Score Spots	1	5.0 (0.0)	4.8 (0.2)	1.0 (0.0)	4.2 (1.1)	2.1 (0.6)
	2					2.4 (0.6)
	3					5.0 (0.0)
Avg. Glass Score Film	1	1.1 (0.2)	4.4 (0.2)	4.1 (0.9)	4.8 (0.2)	4.7 (0.5)
	2					2.3 (0.2)
	3					1.8 (0.4)

(continued)

7-cycle Soil removal	Exp.	Detergent Control 1	Detergent Control 2	Detergent Control 1 + Rinse Aid Control 2	Detergent Control 2 + Rinse Aid Control 1	Exp. 2
Avg. Protein Glass Score	1	1.3 (0.3)	5.0 (0.0)	1.3 (0.3)	5.0 (0.0)	3.5 (0.5)
	2					1.3 (0.3)
	3					2.0 (0.5)
Avg. Protein Plastic Score	1	1.0 (0.0)	5.0 (0.0)	1.0 (0.0)	5.0 (0.0)	1.0 (0.0)
	2					2.0 (0.0)
	3					1.5 (0.0)

**[0197]** These Examples demonstrate that the compositions of the present invention, provided similar, substantially similar, or better performance when compared with existing detergents and existing detergents and rinse aids in most categories of cleaning and antiredeposition in a traditional warewash procedure.

**[0198]** The inventions being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the inventions and all such modifications are intended to be included within the scope of the following claims. The above specification provides a description of the manufacture and use of the disclosed compositions and methods. Since many embodiments can be made without departing from the spirit and scope of the invention, the invention resides in the claims.

### Claims

1. An alkaline detergent and rinsing composition comprising:

from 45 wt-% to 75 wt-% of an alkalinity source comprising an alkali metal carbonate; from 1 wt.-% to 10 wt-% of a nonionic surfactant selected from the group consisting of C8-C18 alcohol ethoxylate with about 10 to about 30 moles of ethylene oxide, an EO/PO represented by the formula (PO)y(EO)x(PO)y, where x is in the range of 5 to 50, y is in the range of 1 to 15, and x plus y is in the range of 6 to 200; and from 5 wt-% to about 50 wt-% of a builder selected from the group consisting of condensed phosphates, alkali metal silicates and metasilicates, phosphonates and aminocarboxylic acids; wherein said composition performs both a cleaning and rinsing function.

45

50

5

10

15

20

25

30

35

- 2. The composition of claim 1, wherein said alcohol alkoxylate and alkyl alkoxylate are in a ratio of between about 3:1 to 1:3
- **3.** The composition of claim 1 or 2, wherein said composition provides substantially similar cleaning and rinsing performance as separate detergent and rinse aid compositions.
  - **4.** The composition of any one of claims 1-3, further comprising a neutralizing agent in an amount between 0.1 wt-% and about 50 wt-%.
- 55 The composition of claim 4, wherein the alkalinity source comprises an alkali metal carbonate, wherein the alkalinity source is substantially free of alkali metal hydroxide, and wherein the neutralizing agent comprises up to about 10 wt-% alkali metal hydroxide.

- **6.** The composition of any one of claims 1-5, further comprising an enzyme.
- 7. The composition of claim 6, wherein the enzyme is a protease, lipase and/or amylase.
- 5 8. The composition of any one of claims 1-7, wherein the builder comprises a phosphonate or aminocarboxylic acid.
  - 9. The composition of any one of claims 1-8, wherein the alkaline detergent is a cast, extruded, or pressed solid.
  - **10.** A method of cleaning and rinsing ware comprising: contacting ware with an alkaline detergent composition of claim 1.

10

15

25

30

35

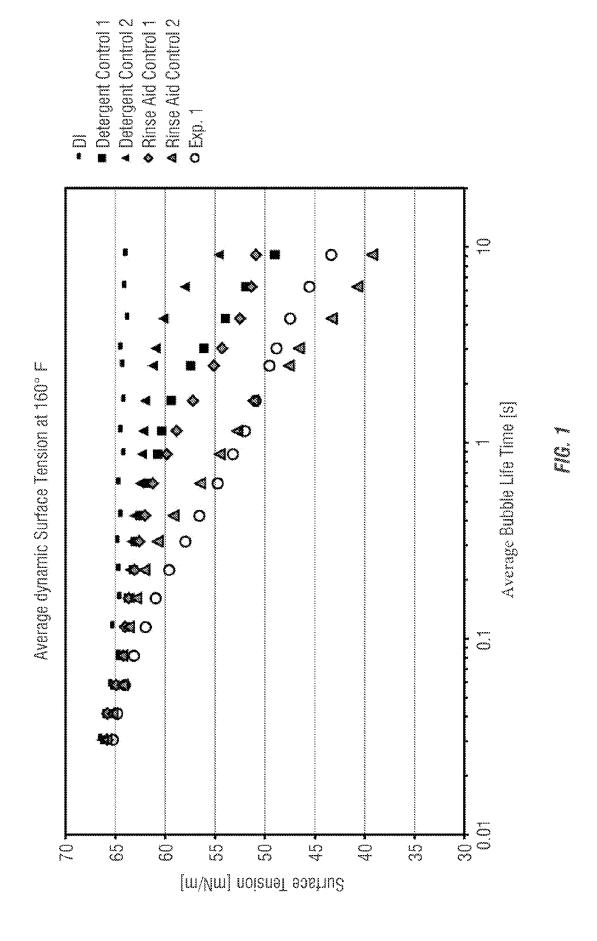
40

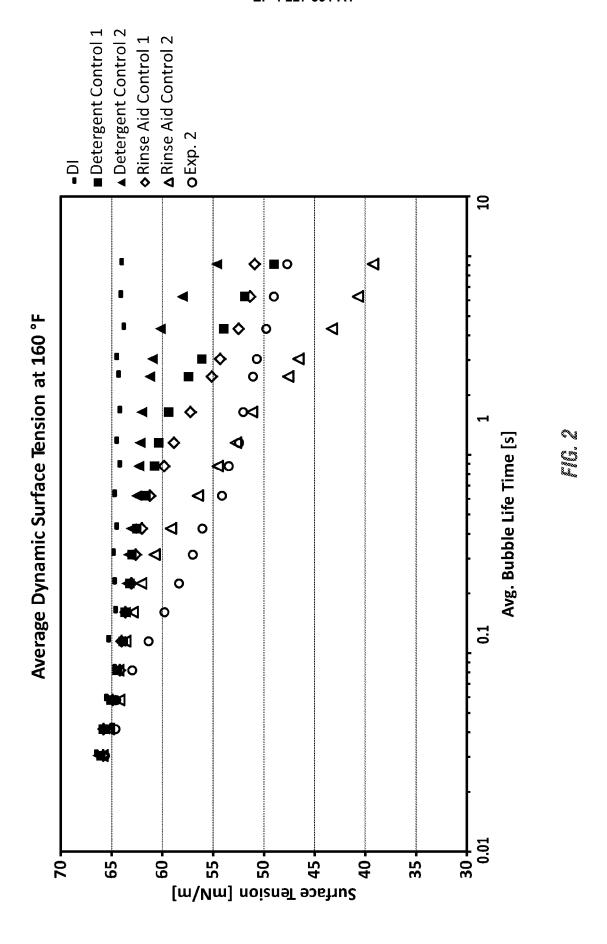
45

50

55

- 11. The method of claim 10, wherein said alcohol alkoxylate and alkyl alkoxylate are in a ratio of between about 3:1 to 1:3
- **12.** The method of claim 10, wherein the alkaline detergent composition further comprises a neutralizing agent in an amount between about 0.1 wt-% and about 50 wt-%.
  - **13.** The method of claim 12, wherein the alkalinity source is substantially free of alkali metal hydroxide, and wherein the neutralizing agent comprises up to about 10 wt-% alkali metal hydroxide.
- 20 **14.** The method of claim 10, wherein the composition further comprises a protease, lipase and/or amylase enzyme.
  - 15. The composition of claim 10, wherein the builder comprises a phosphonate or aminocarboxylic acid.







# **EUROPEAN SEARCH REPORT**

**Application Number** 

EP 23 17 6658

x	of relevant passages  US 6 034 044 A (SCHEPER WILLIAM MICHE [US] ET AL) 7 March 2000 (2000-03-07 * column 5, line 66 - column 6, line * column 24, line 61 - column 25, line * claims; examples *  US 2011/232692 A1 (ZIPFEL JOHANNES [INTERPRETARY NEW MICHE PROPERTARY NEW MICH PROPERTARY NEW MICHE PROPERTARY NEW MICHE PROPERTARY NEW MICH PROPERTARY NEW MICHE PROPERTARY NEW MICHE PROPERTARY NEW MICHE PROPERTARY NEW MICH PROPERTARY NEW MICH PROPERTARY NEW MICHE PROPERTARY NEW MICH PROPERTARY NEW MICH PROPERTARY NEW MICH PROPERTA	AEL 1- ) 31 * ne 34  DE] ET 1-		APPLICATION (IPC)  INV. C11D1/66 C11D3/10 C11D3/37 C11D11/00  ADD. C11D1/00 C11D1/72
x	[US] ET AL) 7 March 2000 (2000-03-07 * column 5, line 66 - column 6, line * column 24, line 61 - column 25, line * claims; examples *	) 31 * ne 34  DE] ET 1-	-15	C11D1/66 C11D3/10 C11D3/37 C11D11/00 ADD. C11D1/00
x	[US] ET AL) 7 March 2000 (2000-03-07 * column 5, line 66 - column 6, line * column 24, line 61 - column 25, line * claims; examples *	) 31 * ne 34  DE] ET 1-		C11D1/66 C11D3/10 C11D3/37 C11D11/00 ADD. C11D1/00
x x	* column 5, line 66 - column 6, line * column 24, line 61 - column 25, line * claims; examples *  " US 2011/232692 A1 (ZIPFEL JOHANNES [INTERPORT 2011 (2011-09-29)] * paragraphs [0002], [0040] - [0127] claims; examples; tables *  " US 2004/167049 A1 (KESSLER ARND [DE] AL) 26 August 2004 (2004-08-26)	31 * ne 34  DE] ET 1-		C11D3/37 C11D11/00 ADD. C11D1/00
x	* claims; examples * US 2011/232692 A1 (ZIPFEL JOHANNES [1 AL) 29 September 2011 (2011-09-29) * paragraphs [0002], [0040] - [0127 claims; examples; tables * US 2004/167049 A1 (KESSLER ARND [DE] AL) 26 August 2004 (2004-08-26)	DE] ET 1-		C11D11/00 ADD. C11D1/00
x x	* claims; examples *	1;		ADD. C11D1/00
x x	US 2011/232692 A1 (ZIPFEL JOHANNES [1 AL) 29 September 2011 (2011-09-29) * paragraphs [0002], [0040] - [0127 claims; examples; tables * US 2004/167049 A1 (KESSLER ARND [DE] AL) 26 August 2004 (2004-08-26)	1;		C11D1/00
x	AL) 29 September 2011 (2011-09-29)  * paragraphs [0002], [0040] - [0127 claims; examples; tables * US 2004/167049 A1 (KESSLER ARND [DE] AL) 26 August 2004 (2004-08-26)	1;		C11D1/00
x	AL) 29 September 2011 (2011-09-29)  * paragraphs [0002], [0040] - [0127 claims; examples; tables * US 2004/167049 A1 (KESSLER ARND [DE] AL) 26 August 2004 (2004-08-26)	1;		
x	* paragraphs [0002], [0040] - [0127 claims; examples; tables * US 2004/167049 A1 (KESSLER ARND [DE] AL) 26 August 2004 (2004-08-26)		15	C11D1//2
x	claims; examples; tables * US 2004/167049 A1 (KESSLER ARND [DE] AL) 26 August 2004 (2004-08-26)		1 5	
x	US 2004/167049 A1 (KESSLER ARND [DE] AL) 26 August 2004 (2004-08-26)	ET 1-	1 5	
	AL) 26 August 2004 (2004-08-26)	ET 1-	1 5	
	AL) 26 August 2004 (2004-08-26)		-13	
	* paragraphs [0006], [0050], [0133			
		1;		
	claims; examples *			
.		ОШВ	1 5	
x	US 2012/167922 A1 (SENDOR-MULLER DORGIDE] ET AL) 5 July 2012 (2012-07-05)	OTA  1-	-15	
	* paragraphs [0010], [0014], [0037	1 -		
	[0106]; claims *	•		TECHNICAL FIELDS
				SEARCHED (IPC)
	US R E38 262 E (ROLANDO JOHN J [US]	ET AL) 1-	-15	C11D
	7 October 2003 (2003-10-07)			
	* column 1, lines 13-21 *			
	* column 8, line 18 - column 9, line	10 *		
	* claims; examples *			
x	DE 200 14 919 U1 (HENKEL KGAA [DE])	1-	-15	
	30 November 2000 (2000-11-30)			
	* page 1, lines 1-3 *			
	$\star$ page 3, line 30 - page 4, line 8 $\star$			
	* page 8, lines 18-24 *			
	* page 26, lines 1-22 *  * claims; examples *			
	- Claims; examples *			
	-/			
	·			
	The consent county is a second to a second county in the second county is a second county in the second county in the second county is a second county in the second county in the second county is a second county in the second county in the second county is a second county in the se			
	The present search report has been drawn up for all claims		1	
	Place of search Date of completion of th			Examiner
	Munich 12 July 20	23	Pén	tek, Eric
CA	ATEGORY OF CITED DOCUMENTS  T: theory	y or principle und er patent docume	derlying the i	nvention
X : parti	cularly relevant if taken alone after t	the filing date		arred Off, Of
docu	iment of the same category L: docur	ment cited in the ment cited for oth	ner reasons	
		ber of the same		r, corresponding

page 1 of 2



# **EUROPEAN SEARCH REPORT**

Application Number

EP 23 17 6658

10	

	DOCUMENTS CONSIDERED		1	
Category	Citation of document with indicatio of relevant passages	n, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
x	US 2004/254090 A1 (LENT ET AL) 16 December 2004 * paragraphs [0002], [ [0037]; claims; example	(2004-12-16) 0003], [0035],	1-15	
х	US 2007/082836 A1 (BOTH 12 April 2007 (2007-04- * paragraphs [0003], [ [0043] - [0047]; claims	1-15		
х	US 2010/065090 A1 (TROP 18 March 2010 (2010-03- * paragraphs [0001], [ [0220]; claims; example	18) 0007], [0008],	1–15	
х	US 5 612 305 A (LEWIS R 18 March 1997 (1997-03- * column 1, lines 8-15;	18)	1-15	
x	US 4 233 171 A (MCLAUGH 11 November 1980 (1980- * column 4, lines 39-68 *	11-11)	1-15	TECHNICAL FIELDS SEARCHED (IPC)
x	US 2010/311633 A1 (JOHN AL) 9 December 2010 (20 * paragraphs [0002], [ examples *	10-12-09) 0009]; claims;	1–15	
х	EP 0 687 720 A2 (BASF C 20 December 1995 (1995- * page 2, line 1 - page tables *	ORP [US]) 12-20)	1–15	
x	DE 197 32 689 A1 (BASF 4 February 1999 (1999-0		1-9	
A	* page 8, lines 11-12;	examples * 	10-15	
	The present search report has been do	awn up for all claims	_	
	Place of search	Date of completion of the search	1	Examiner
	Munich	12 July 2023	Pén	tek, Eric
X : part Y : part doci A : tech	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with another ument of the same category inological background		cument, but publi te n the application or other reasons	shed on, or
	-written disclosure rmediate document	& : member of the s document	ame patent family	, corresponding

page 2 of 2

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 17 6658

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-07-2023

	Patent document ted in search report		Publication date		Patent family member(s)		Publication date
US	6034044	A	07-03-2000	AT	254162	T	15-11-200
				AU	4412697	A	02-04-199
				BR	9712813	A	23-11-199
				CA	2265825	A1	19-03-199
				DE	69726165	Т2	02-09-20
				EP	0927237	<b>A1</b>	07-07-19
				ES	2210578	т3	01-07-20
				JP	2002502445	A	22-01-20
				US	6034044	A	07-03-20
				WO	9811187	A1	19-03-19
US	2011232692	A1	29-09-2011	DE	102008060471	A1	10-06-20
				EP	2358853	A1	24-08-20
				ES	2622984	т3	10-07-20
				PL	2358853	т3	31-08-20
				US	2011232692	A1	29-09-20
				WO	2010063690	A1	10-06-20
US	2004167049	A1	26-08-200 <b>4</b>	AT	392463	т	15-05-20
				DE	10136002	A1	13-02-20
				EP	1409625	A1	21-04-20
				ES	2301669	т3	01-07-20
				HU	0401494	A2	28-12-20
				$_{ t PL}$	198600	в1	31-07-20
				US	2004167049	A1	26-08-20
				WO	03010263	A1	06-02-20
US	2012167922	A1	05-07-2012	DE	102009029637	A1	24-03-20
				EP	2480645	A1	01-08-20
				KR	20120083347	A	25-07-20
				US	2012167922	A1	05-07-20
				WO	2011032868	A1	24-03-20
US	RE38262	E	07-10-2003	AR	011084	A1	02-08-20
				AU	740960	B2	15-11-20
				BR	9714652	A	03-10-20
				CA	2277298	A1	30-07-19
				CN	1245524	A	23-02-20
				DE	69726605	Т2	04-11-20
				EP	0956331	A1	17-11-19
				JP	4621175	B2	26-01-20
				JP	2001505614	A	24-04-20
				JP	2006336019	A	14-12-20
				MY	115567	A	31-07-20
				TW	404980	В	11-09-20
				US	5876514	A	02-03-19

page 1 of 3

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 17 6658

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-07-2023

	Patent document ed in search report		Publication date		Patent family member(s)		Publication date
		'		US	RE38262	E	07-10-20
				WO	9832823	A1	30-07-19
				ZA	979936	В	05-05-19
DE	20014919	U1	30-11-2000	NON	·————————————————————————————————————		
US	2004254090	A1	16-12-2004	AR	015341	A1	02-05-20
				AU	739007	B2	04-10-20
				BR	9806734	A	29-02-20
				CA	2277029	A1	16-07-19
				CN	1243537	A	02-02-20
				EP	0971996	A1	19-01-20
				ID	22452	A	14-10-19
				JP	4166836	B2	15-10-20
				JP	2001508111	A	19-06-20
				KR	20010049155	A	15-06-20
				MΥ	120961	A	30-12-20
				NZ	336349	A	22-12-20
				TW	408175	В	11-10-20
				US	6164296	A	26-12-20
				US	6489278	в1	03-12-20
				US	6664219	в1	16-12-20
				US	2004087459	A1	06-05-20
				US	2004254090	A1	16-12-20
				US	2006040841	A1	23-02-20
				WO	9830662	A1	16-07-19
				ZA	9710544 	В 	24-05-19 
US	2007082836	A1	12-04-2007	DE	102005044028	A1	15-03-20
				EP	1764408	A1	21-03-20
				ES	2343074	т3	22-07-20
				US 	2007082836	A1 	12-0 <b>4</b> -20
US	2010065090	<b>A1</b>	18-03-2010	CA	2684069	A1	06-11-20
				CN	101688156	A	31-03-20
					102007019457		30-10-20
				EP	2148917		03-02-20
				JP	5595262		24-09-20
				JP	2010525127		22-07-20
				KR	20100017375		16-02-20
				US	2010065090		18-03-20
				WO	2008132131	A1 	06-11-20 
US	5612305	A	18-03-1997	CA			13-07-19
				US	5612305	A	18-03-19

page 2 of 3

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 17 6658

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-07-2023

	cite	Patent document ed in search report		Publication date		Patent family member(s)	Publication date
	ບຣ	4233171	A	11-11-1980	CA US	1131094 4233171	07-09-1982 11-11-1980
	us	2010311633	A1	09-12-2010	NONE		 
	EP	0687720	A2	20-12-1995	NONE		
	DE 	19732689 	A1	0 <b>4</b> -02-1999	NONE		 
M P0459				fficial Journal of the Euro			
C FORM							

page 3 of 3

#### REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

### Patent documents cited in the description

- US RE38262 E [0003]
- US 3929678 A, Laughlin and Heuring [0045] [0090] [0096]
- US 6436893 B [0062]
- US 3048548 A, Martin [0077]
- US 3334147 A, Brunelle [0077]
- US 3442242 A, Rue [0077]
- US 8889048 B **[0115]**
- US 7153820 B [0119]
- US 7094746 B [0119]
- US 7087569 B [0119]
- US 7037886 B [0119]
- US 6831054 B **[0119]**
- US 6730653 B [0119]
- US 6660707 B [0119]

- US 6653266 B [0119]
- US 6583094 B [0119]
- US 6410495 B [0119]
- US 6258765 B [0119]
- US 6177392 B [0119]
- US 6156715 A [0119]
- US 5858299 A [0119]
- US 5316688 A [0119]
- US 5234615 A [0119]
- US 5198198 A [0119]
- US 5078301 A [0119]
- 00 0070001 A [0119]
- US 4595520 A [0119]
  US 4680134 A [0119]
- US RE32763 A [0119]
- US RE32818 A [0119]

### Non-patent literature cited in the description

- Nonionic Surfactants. Surfactant Science Series.
   Marcel Dekker, Inc, 1983, vol. 1 [0045]
- SCHWARTZ; PERRY; BERCH. Surface Active Agents and detergents, vol. I, II [0045]
- KIRK-OTHMER. Encyclopedia of Chemical Technology. vol. 5, 339-366 [0061]
- KIRK-OTHMER. ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. vol. 23, 319-320 [0061]
- Industrial Enzymes. SCOTT, D. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, 1980, vol. 9, 173-224 [0073]
- Surfactant Encyclopedia. Cosmetics & Toiletries, 1989, vol. 104 (2), 69-71 [0084]
- SCHWARTZ; PERRY; BERCH. Surface Active Agents and Detergents, vol. I,II [0090] [0096]