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(54) Rinse aid composition and method for using the same

(57) A rinse aid composition that does not inhibit starch breakdown and a cleaning system using the same is described. The rinse aid composition comprises a surfactant which when contacted with a gelled azure starch that is subsequently retrograded and suspended in a detergent wash having a compound capable of causing starch degradation, does not prevent at least about 75% degradation of the suspended azure starch present in the detergent wash or the rinse aid composition does not result in a washed ceramic tile coated with a potato starch from displaying a $\%\Delta R$ of greater than about 24, or both.

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Description

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FIELD OF THE INVENTION

[0001] This invention relates to a novel rinse aid composition and a method for using the same. More particularly, the invention is directed to a method for using a superior rinse aid composition in dishwashing systems that unexpectedly results in dishware that does not display starch build-up after washing.

BACKGROUND OF THE INVENTION

[0002] Traditional industrial and domestic dishwashing systems rely on a combination of high alkalinity and chlorine bleach for cleaning and sanitizing dishware. Such systems perform extremely well on bleachable stains; however, they tend to be deficient in removing starchy soils like those often found on dishware in domestic kitchens, hospitals, cafeterias, catering industries and the like.

[0003] Other attempts have been made to create dishwashing systems that are effective at handling starchy soils. These systems typically employ commercially available enzymes that break down the starchy soil in the various cycles of the dishwashing systems they are employed in. The enzymes used in systems for treating starchy soils on dishware are generally not limited and include those which typically break or hydrolyze the α -1,4-glycosidic linkages of the starch backbone

[0004] In addition to being sanitized, it is very desirable for dishware exiting dishwashing systems to be dry with a glossy finish. These characteristics are often achieved by employing a rinse aid composition in the final rinse step of the dishwashing system.

[0005] Unfortunately, however, it has been discovered that, while the use of rinse aid compositions typically results in dishware with appealing characteristics, such use also can interfere with the removal of starchy soils from the dishware being cleaned. In fact, studies indicate that rinse aid compositions can result in poor starch removal on dishware subject to as little as one cleaning cycle.

[0006] It is of increasing interest to develop rinse aid compositions that maintain their conventional characteristics and do not adversely interfere with the cleaning process of a dishwashing system. Also, it is of increasing interest to develop methods that prevent starch build-up on articles, such as dishware, being cleaned. The inventions described herein, therefore, are directed to a superior rinse aid composition and a method for preventing starch build-up on articles. The inventions unexpectedly result in a clean article that is dry with a glossy finish and substantially free of starch build-up upon exiting a cleaning system, like a dishwashing system. Moreover, the present inventions not only prevent starch build-up on articles being cleaned, the inventions simultaneously do not interfere with the normal drying time of the articles being cleaned.

DESCRIPTION OF BACKGROUND REFERENCES

[0007] Attempts have been made to prepare rinse aid compositions for cleaning systems.

[0008] In US-A-5,827,451, a microemulsion useful as a rinse aid composition is disclosed, and the microemulsion comprises an oil component of a fatty acid.

[0009] Other attempts for making rinse aid compositions have been disclosed. In US-A-5,821,212, rinse aid compositions with hydrogen peroxide are disclosed.

[0010] Further, in US-A-5,953,608, rinse aid compositions comprising nonionic surfactants, acrylic acid polymers and phosphate esters are disclosed.

5 **[0011]** Still further, in US-A-5,691,300, rinse aid compositions having fatty acid N-alkyl polyhydroxyalkyl amides are disclosed.

[0012] Finally, in US-A-5,739,099, rinse aid compositions with copolymers of alkylene oxide, adducts of allyl alcohol and acrylic acid are disclosed.

[0013] The prevention of starch build-up on articles being cleaned has not been addressed in the above-described references. The present inventions, therefore, are patentably distinguishable from the above-described since, among other reasons, they are directed to the prevention of starch build-up on articles being cleaned in a variety of systems, and especially, a dishwashing system.

SUMMARY OF THE INVENTION

[0014] In a first embodiment, this invention is directed to a superior rinse aid composition. The rinse aid composition is compatible with cleaning systems, like dishwashing systems, designed for removing starchy soils. The rinse aid composition, which prevents starch build-up, comprises at least one surfactant selected from the group consisting of a non-

ionic and anionic surfactant, and the rinse aid composition, when contacted with gelled azure starch that is subsequently retrograded and suspended in a detergent wash having a compound capable of causing starch degradation, does not prevent at least about 75% degradation of the suspended azure starch present in the detergent wash as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled form, was not contacted with the rinse aid composition, or the rinse aid composition, when contacted with a washed ceramic tile originally and uniformly soiled with potato starch, does not cause the washed ceramic tile originally and uniformly soiled with potato starch to display a % ΔR of more than about 24 as determined by monitoring reflectance at 460 nm of a ceramic tile wherein the ceramic tile:

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- (a) is about 5.7 cm²;
- (b) is, on three occasions, uniformly coated with about 1.0g of potato starch, air dried, washed for about three minutes in a detergent wash at about 65°C and rinsed for about 30 seconds with the rinse aid composition, said detergent wash comprising enough starch degrading material to yield, in no more than about three minutes, a ceramic tile displaying a % Δ R of about 5 wherein the ceramic tile displaying a % Δ R of about 5.7 cm², is, on three occasions uniformly coated with about 1.0 gram of potato starch, washed for about three minutes in the detergent wash and not subjected to the rinse aid composition;
- (c) is submerged, for about 5 seconds, in a solution comprising about 1.5% by weight potassium iodide and about 0.2% by weight iodine, rinsed with deionized water and air dried for about 15 minutes,

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or both.

[0015] In a second embodiment, this invention is directed to a cleaning system having the above-described rinse aid composition.

[0016] In a third embodiment, this invention is directed to a method for preventing starch build-up by using the above-described rinse aid composition.

[0017] As used herein, % starch degradation is equal to $A_s/A_i \times 100$ wherein A_s is the absorbance at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch that has been subjected to the rinse aid composition of this invention and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch, when in its gelled form has not been contacted with the rinse aid composition of this invention, and A_i is the absorbance at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch that has not been subjected to the rinse aid composition of this invention and enough compound capable of degrading, in no more than a bout 30 minutes, about 1.25 grams of azure starch, when in its gelled form has not been contacted with the rinse aid composition of this invention. Further, as used herein, rinse aid composition is defined to mean 0.0375 grams per liter surfactant, either in the neat or via a 0.25 grams per liter rinse aid having 15% surfactant.

[0018] As used herein %∆R is equal to (Rw-Ri)/(Rs-Ri)

R_w = Reflectance of a tile after three soil wash-rinse cycles

R_i = Reflectance of a clean tile before soiling

R_s = Reflectance of a soiled tile before washing

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] There is generally no limitation with respect to the form the rinse aid composition of this invention takes other than that the rinse aid composition is capable of being used in a cleaning system such as a dishwashing system. Therefore, it is within the scope of this invention for the rinse aid composition to, for example, be a solid, liquid, gel or slurry. In the solid form, the rinse aid composition is often a tablet, block or powder. Preferably, however, the rinse aid composition of this invention is in liquid form.

[0020] When preparing the rinse aid composition of this invention, the composition often comprises at least about 5.0% by weight surfactant, and preferably, at least about 10.0% by weight surfactant, and most preferably, at least about 20.0% by weight surfactant, (not to exceed about 70.0% by weight) based on total weight of the rinse aid composition, and including all ranges subsumed therein. In addition to surfactant, the rinse aid composition of this invention may also comprise conventional additives which include water, acids and alcohols. Other conventional additives which may be employed in the rinse aid composition of this invention include defoaming agents, hydrotropes, chelators, preservatives, hydroxides, buffers, bleach scavengers, flow control agents, colorants, anti-microbial agents, anti-scalants, anti-corrosion agents and the like.

[0021] The only limitation regarding the type of surfactant used is that the surfactant results in a rinse aid composition which, when contacted with gelled azure starch that is subsequently retrograded and suspended in a detergent

wash having a compound capable of causing starch degradation, does not prevent at least about 75% degradation of the suspended azure starch present in the detergent wash as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled form, was not contacted with the rinse aid composition, or the rinse aid composition, when contacted with a washed ceramic tile originally and uniformly soiled with potato starch, does not cause the washed ceramic tile originally and uniformly soiled with potato starch to display a % ΔR of more than about 24 as determined by monitoring reflectance at 460 nm of a ceramic tile wherein the ceramic tile:

- 10 (a) is about 5.7 cm²;
 - (b) is, on three occasions, uniformly coated with about 1.0g of potato starch washed for about three minutes in a detergent wash at about 65°C and rinsed for about 30 seconds with the rinse aid composition, said detergent wash comprising enough starch degrading material to yield, in no more than about three minutes, a ceramic tile displaying a % Δ R of about 5 wherein the ceramic tile displaying a % Δ R of about 5.7 cm², is, on three occasions uniformly coated with about 1.0 gram of potato starch, washed for about three minutes in the detergent wash and not subjected to the rinse aid ;
 - (c) is submerged, for about 5 seconds, in a solution comprising about 1.5% by weight potassium iodide and about 0.2% by weight iodine, rinsed with deionized water and air dried for about 15 minutes,

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[0022] Preferably, however, the surfactants result in a rinse aid composition which, when contacted with gelled azure starch that is subsequently retrograded and suspended in a detergent wash having a compound capable of causing starch degradation, does not prevent at least about 85% degradation, and most preferably, does not prevent at least about 90% degradation of suspended azure starch as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled form, was not contacted with the rinse aid composition, or preferably, the surfactants result in a rinse aid composition which, when contacted with a washed ceramic tile soiled with potato starch, does not cause the washed ceramic tile to display a % Δ R of more than about 20, and preferably, does not cause the washed ceramic tile to display a % Δ R of more than about 18 under the above-outlined conditions, or both.

[0023] When selecting the surfactant to yield the superior rinse aid composition that prevents starch build-up of this invention, it is important to consider the alkyl chain length of the surfactant employed as well as the nature of the hydrophobe (e.g., branching). It is also important to consider the hydrophilic head groups on the surfactant. It has been unexpectedly discovered that by considering such characteristics of the surfactant, the amount of residual amylose remaining on articles at the end of a wash is substantially eliminated. The substantial elimination of residual amylose on washed articles inevitably results in cleaned articles (like dishes) having a dry, glossy finish, even after being subjected to a cleaning system, like a dishwashing system, on one or multiple occasions.

[0024] The nonionic surfactant which may be employed in this invention includes those which may be generally classified as fatty acid or alcohol condensates. Broadly, the nonionic surfactant may be defined, for example, as a compound produced by the condensation of alkylene oxide groups (hydrophilic groups) with an organic compound having a hydrophobic group. Such a nonionic surfactant is commercially available from, for example, Uniqema, Henkel Kommanditgesellschaft auf Atkien, Shell Chemical Company, Union Carbide, Condea, Stepan and BASF. Many of the nonionic surfactants which may be used in this invention are sold under the names Neodol[®], Plurafac[®], Dehypon and Synperonic. It is also noted herein that derivatives of the commercially available nonionic surfactants may be employed in this invention.

[0025] Illustrative examples of other nonionic surfactants which may be employed in this invention include those generally made from precursor heterocyclic or aromatic compounds that have been subjected to, for example, condensation reactions resulting in ester substituents, or ammonia resulting in amide substituents. Many of these nonionic surfactants are commercially available from, for example, Uniqema, Nippon Youshi, Toho Chemical and Dow. They are typically sold under the names Tween[®], Arlecel[®], and Glucopon[®], and use of derivatives of these commercially available surfactants is also within the scope of this invention.

[0026] A more detailed description of the general types of surfactants which may be employed in the rinse aid composition of this invention includes those described in US-A-5,741,767.

[0027] The preferred nonionic surfactant which may be employed in the superior rinse aid composition of this invention is often represented by at least one structural formula selected from the group consisting of:

$$R = \begin{pmatrix} R & R^{1} & R^{2} & R^{2} \\ C & C & C & C \\ R & R & P \end{pmatrix} \begin{pmatrix} R^{2} & R^{2} & R^{2} \\ C & C & C \\ R^{2} & R^{2} & R^{2} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{2} \\ R^{2} & R^{2} & R^{2} & R^{2} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{2} & R^{2} & R^{2} & R^{2} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{2} & R^{2} & R^{2} & R^{2} & R^{3} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{2} & R^{2} & R^{2} & R^{3} & R^{3} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} & R^{3} & R^{3} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} & R^{3} & R^{3} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} & R^{3} & R^{3} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} & R^{3} & R^{3} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} & R^{3} & R^{3} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} & R^{3} & R^{3} \end{pmatrix} \begin{pmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} & R^{3} & R^{3} & R^{3} \end{pmatrix}$$

HO—C—C—C—C—C—C—N—R⁶
R OH Q R OH

, and

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- a) each R is independently a hydrogen, C₁ alkyl, hydroxy or alkoxy;
- b) each R¹ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- c) each R² is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- d) each R³ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, C₁₋₄ halocarbon, hydroxy or alkoxy;
- e) p is an integer from about 1 to about 20, preferably about 6 to about 20, and q is an integer from about 0 to about 20, preferably about 6 to about 20, and each t is independently an integer from about 1-5;
- f) each R⁴ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- g) R⁵ is a C₁-C₁₅ alkyl or aryl;
- h) each R⁶ is independently a hydrogen, C₁-C₁₅ alkyl, aryl hydroxy or alkoxy;
- i) each R⁷ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- j) each R⁸ is independently a hydrogen, C₁₋₄ alkyl, C₁₋₄ halocarbon, hydroxy or alkoxy;
- k) each R^9 is independently a hydrogen, $C_{1\text{--}20}$ alkyl, aryl or $C_{1\text{--}4}$ halocarbon;
- I) n is an integer from about 2 to about 40, and
- m) w is an integer from about 0 to about 3.

[0028] Often, each R^1 and each R^2 are not simultaneously hydrogen and each R^6 is not simultaneously hydrogen, and at least about 50% of all units represented as q have at least one R^2 as a C_1 - C_{15} alkyl or aryl when each R^1 is hydrogen and each t is 1. Preferably, at least about 55%, and most preferably, at least about 60% of all units represented as q have at least one R^2 as a C_1 - C_{15} alkyl or aryl when each R^1 is hydrogen and each t is 1. Thus, it is noted herein that each unit represented as q may be identical or different and q may be a random or block portion of formula I. [0029] In a most preferred embodiment, the superior rinse aid composition of this invention will have a first surfactant represented by formula I wherein each R is hydrogen, R^1 is hydrogen, R^1 is an integer from about 11 to about 14, t is 1, q is 8 with a block of 3 ethylene oxide units and a block of 5 propylene oxide units and R^3 is a hydrogen, and a second surfactant represented by formula I wherein each R^1 is hydrogen, R^1 is hydrogen, R^1 is hydrogen, R^2 is an integer from about 11 to about 14, t is 1, q is 10 with a block of 5 ethylene oxide units and a block of 5 propylene oxide units and R^3 is a hydrogen. The first surfactant and second surfactant are sold under the names Synperonic LF/RA270 and Synperonic LF/RA280, respectively, and commercially available from Uniqema. The amount of first surfactant to second surfactant employed in the rinse aid composition is not limited, but about 25% to about 100% by weight more of the second surfactant is preferred, based on total weight of first and second surfactant in the rinse aid composition.

[0030] The anionic surfactants which may be employed in the rinse aid compositions of this invention include those having a sulfate, phosphate ester or sulfonate group. Such anionic surfactants are often made via conventional processes known in the art. These anionic surfactants are often commercially available from, for example, Stepan Chemical and Dow. Some of the anionic surfactants which may be used in this invention are sold under the name Dowfax[®]. It is also noted herein that derivatives of these commercially available anionic surfactants may be employed in this invention.

[0031] The preferred anionic surfactant which may be employed in the superior rinse aid composition of this invention is often represented by at least one structural formula selected from the group consisting of:

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 $SO_3^-\chi^+$, and (VI)

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$$R = \begin{pmatrix} R^{10} \\ C \\ C \\ R^{10} \\ R \end{pmatrix} = \begin{pmatrix} R^{10} \\ R^{$$

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wherein each Ar is independently a monocyclic or polycyclic aromatic radical and each X^+ is an alkali metal, alkaline earth metal or NH_4^+ , and each R^{10} is independently a hydrogen, C_1 - C_{15} alkyl or an aryl, and r is an integer from about 2 to about 8.

[0032] The preferred conventional additives which may be used in the rinse aid compositions of this invention include hydroxy acids, alcohols, hydrotropes, preservatives and water. The hydroxy acids which may be employed in this invention include those that are naturally occurring and commercially available. Often, when preparing the rinse aid compositions of this invention, about 0.0% to about 50.0%, and preferably, from about 5.0% to about 40.0%, and most preferably, from about 10.0% to about 30.0% by weight of hydroxy acid is employed based on total weight of the rinse aid composition, including all ranges subsumed therein. An illustrative list of the hydroxy acids which may be used in this invention include malic acid, lactic acid, citric acid, glycollic acid, tartaric acid and the like. Citric acid, however, is often the most preferred hydroxy acid.

[0033] The alcohols which may be employed in this invention include, for example,

C₁-C₈ primary, secondary or tertiary alcohols. Such alcohols are commercially available. Isopropanol, however, is often the most preferred alcohol. When alcohols are employed in rinse aid compositions, the rinse aid compositions often employ from about 0.0% to about 20.0%, and preferably from about 0.5% to about 10.0% and most preferably from about 1.0% to about 5.0% by weight alcohol based on total weight of the rinse aid composition.

[0034] The hydrotropes which may be employed in this invention are limited only to the extent that they enhance the solubility of the surfactants in the superior rinse aid compositions of this invention. The hydrotropes which may be used in this invention are those which are commercially available, and an illustrative list includes sodium xylene sulfonate, sodium cumene sulfonate, hexylene glycol, propylene glycol, dihexyl sodium sulfonate and low molecular weight sulfate. Other useful hydrotropes which may be employed in this invention include those described in U.S. Patent Nos. 3,563,901 and 4,443,270, the disclosures of which are incorporated herein by reference.

[0035] When hydrotropes are employed in the superior rinse aid compositions of this invention, they often represent from about 0.1% to about 20.0%, and preferably, from about 2.0% to about 15.0%, and most preferably, from about 5.0% to about 12.0% by weight of the total weight of the rinse aid composition, including all ranges subsumed therein.

[0036] The preservatives which may be used in the rinse aid composition of this invention include ascorbic acid, erythorbic acid, sorbic acid, thiodipropionic acid, ascorbyl palmitate, butylated hydroxyamisol, butylated hydroxytolu-

ene, calcium ascorbate, calcium sorbate, dilauryl thiodipropionate, potassium bisulfate, potassium metabisulfate, potassium sorbate, sodium ascorbate, sodium bisulfate, sodium meta bisulfite, sodium sorbate, sodium sulfite, sulfur dioxide, tocophenols and Group IA and IIA salts, with potassium chloride being preferred. When preservatives are used in the rinse aid compositions of this invention, they typically make up about 0.01% to about 0.2%, and preferably, from about 0.02% to about 0.1%, and most preferably, from about 0.04% to about 0.8% by weight of the total rinse aid composition, including all ranges subsumed therein.

[0037] When water is employed in the rinse aid composition of this invention, it generally is the solvent making up the balance of the rinse aid composition.

[0038] The superior rinse aid compositions of this invention may be prepared via any of the art recognized techniques. Essentially, the components (e.g., surfactant, water, alcohol) of the rinse aid composition are, for example, mixed, stirred or agitated. The rinse aid composition of this invention may be made at ambient temperature, atmospheric pressure or at any pressure or temperature variations which may result in the rinse aid compositions of this invention. The addition of the components is not limited to any particular order, with the proviso that the resulting composition is one which may be employed as a rinse aid composition that prevents starch build-up in cleaning systems.

[0039] It is particularly noted that the total amount of surfactant used in the rinse aid composition of this invention may comprise, consist essentially of, or consist of the nonionic and anionic surfactants described in formulae (I) through (VII).

[0040] The cleaning system which comprises the superior rinse aid composition of this invention is limited only to the extent that the cleaning system is one which has the general objective of producing a clean article that is dry with a glossy finish and free of starch build-up. Therefore, the cleaning system which may employ the rinse aid composition of this invention includes systems for cleaning kitchens and dishware. The preferred cleaning system which comprises the rinse aid composition of this invention is, however, a dishwashing system.

[0041] The dishwashing system which may use the rinse aid composition of this invention is not limited and includes those which usually have at least one prewash, wash and rinse step. The actual hardware involving the dishwashing system which may use the rinse aid composition of this invention is not limited and includes dishwashing machines that are conventionally used in household kitchens as well as those which may be classified as single or multi-tank industrial warewashing machines and conveyor-type machines.

[0042] In a preferred embodiment, the dishwashing system which uses the superior rinse aid composition of this invention also uses a detergent wash. The detergent wash which may be used in this invention is generally not limited, and preferably, is one that comprises at least one compound capable of causing starch degradation. The compound which is capable of causing starch degradation is only limited to the extent that it is a compound which is capable of hydrolyzing the glycosidic linkages of starch or breaking any of the sp^3 bonds of the glucose monomers that make up the starch backbone. Typically, the compounds which are used for starch degradation in the detergent washes which may be employed in this invention are generally classified as enzymes, caustic agents, and oxidizing agents, whereby the oxidizing agents may be used with catalysts. The enzymes which may be used for starch degradation in the detergent washes used in this invention include α -amylase enzymes such as those made commercially available from Novo Industries and Genencor and sold, for example, under the names of Purafect OxAm, Termamyl[®] and Duramyl[®].

[0043] When a detergent wash is prepared that comprises an enzyme, such as amylase, the amount of enzyme typically used in the formulation is such that the final use composition of said enzyme component has an enzyme activity of from about 10 to about 10⁸ Maltose Units/kilogram, and preferably, from about 10² to about 10⁶ MU/kg, and preferably, from about 10² to about 10⁴ MU/kg.

[0044] The enzyme activity as referred to herein can be determined by the method as described by P. Bernfeld in "Method of Enzymology", Volume I (1955), page 149, the disclosure of which is incorporated herein by reference. Other additives which may be employed in the enzymatic detergent washes which may be used in this invention include disilicates, such as sodium disilicate, soda ash, triphosphates like sodium triphosphates, chelators like nitriloacetic acid, polycarboxylates such as sodium polycarboxylate, water, fatty acid alcoxylates and alcohol phosphate ester-type defoaming agents. A more detailed description of the detergent washes (which comprise enzymes) that may be used in this invention are described in US-A- Nos. 5,695,575, 5,741,767 and 5,877,134, the disclosures of which are incorporated herein by reference.

[0045] Detergent washes comprising caustic agents (e.g., NaOH, KOH) that may be used in this invention typically comprise detergent comprising from about 10% to about 75% by weight caustic agent, and preferably, from about 20% to about 65% by weight caustic agent, and most preferably, from about 45% to about 55% by weight caustic agent, based on total weight of the detergent, including all ranges subsumed therein. Other additives which may be employed in the detergent washes comprising caustic agents that may be used in this invention include chelators like nitrilotriacetic acid, water and acids like aminomethylene phosphonic acid and gluconic acid. A more detailed description of the detergent washes with caustic agents that may be used in this invention include those described in U.S. Patent No. 4,774,014, the disclosure of which is incorporated herein by reference.

[0046] The oxidizing agents which may be used in the detergent washes employable in this invention include hydrogen peroxide, chlorine bleach and organo peroxy acids such as those described in U.S. Patent No. 5,741,767, the dis-

closure of which has been incorporated herein by reference.

[0047] The catalysts which may be used in the detergent washes employable in this invention include, for example, those which are broadly classified as metal containing catalysts that enhance oxidizing agents in breaking the sp³ bonds of a glucose ring. Illustrative examples of the preferred metal containing catalyst include those based on manganese, iron, cobalt, titanium, molybdenum, nickel, chromium, copper, ruthenium, tungsten, silver and mixtures thereof. Those include simple water-soluble salts such as those of iron, manganese and cobalt as well as catalysts containing complex ligands.

[0048] Suitable examples of manganese catalysts containing organic ligands are described in U.S. Patent No. 4,728,455, U.S. Patent No. 5,114,606, U.S. Patent No. 5,153,161, U.S. Patent No. 5,194,416, U.S. Patent No. 5,227,084, U.S. Patent No. 5,244,594, U.S. Patent No. 5,246,612, U.S. Patent No. 5,246,621, U.S. Patent No. 5,256,779, U.S. Patent No. 5,274,147, U.S. Patent No. 5,280,117 and European U.S. Patent No. Application Pub. Nos. 544,440, 544,490, 549,271 and 549,272. Preferred examples of these catalysts include ${\rm Mn}^{IV}_{2}(\mu-{\rm O})_{2}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_{2}({\rm CIO}_{4})_{2}, {\rm Mn}^{IV}_{4}(\mu-{\rm O})_{6}(1,4,7\text{-triazacyclononane})_{4}({\rm CIO}_{4})_{4}, {\rm Mn}^{III}_{Mn}^{IV}_{4}(\mu-{\rm O})_{1}(\mu-{\rm OAc})_{2}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_{2}({\rm CIO}_{4})_{3}, {\rm Mn}^{IV}_{1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_{2}({\rm CIO}_{4,1})_{2}, {\rm Mn}^{IV}_{1,4,7\text{-trimeth$

[0049] The metal containing catalyst is used in combination with the oxidizing agent to enhance or catalyse the oxidizing agent's ability to break the sp³ bonds of the glucose rings present in the starch backbone. Typically, the amount of catalyst used is from about 0.05 to about 5.0 weight percent, and preferably, from about 0.05 to about 2.0 weight percent, and most preferably from about 0.075 to about 0.4 weight percent metal containing catalyst based on total weight of the detergent wash, including all ranges subsumed therein. A more detailed description of the types of metal catalysts which may be used in this invention includes those described in U.S. Patent No. 5,900,395, the disclosure of which is incorporated herein by reference.

[0050] When conducting the method for preventing starch build-up on articles in this invention, the method comprises the steps of:

a) cleaning an article; and

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b) subjecting the article to the rinse aid composition described above.

[0051] When conducting the method of this invention, the article being cleaned (e.g., knife, glass mug, cup, china, dishes or plastic kitchen utensils) in, for example, a dishwasher, is often subjected to at least one cycle selected from the group consisting of a presoak cycle, a wash cycle and a rinse cycle, followed by a final rinse cycle which utilizes the superior rinse aid composition of this invention. The final rinse cycle is typically run for about 5 seconds to about 60 seconds in industrial systems and for about 60 seconds to about 5 minutes in domestic systems, and preferably, for about 6 seconds to about 30 seconds, in industrial systems and 75 seconds to 4 minutes in domestic systems, and most preferably, from about 7 seconds to about 12 seconds, in industrial systems and from about 85 seconds to 15 minutes in domestic systems, including all ranges subsumed therein. The temperature of the final rinse is usually from about ambient to about 95°C, and preferably, from about 30°C to about 85°C, and most preferably, from about 40°C to about 75°C, including all ranges subsumed therein, whereby the articles being cleaned are typically dipped in, or preferably, sprayed with the final rinse which comprises the superior rinse aid composition of this invention. The final result of such a method is a clean article with a glossy finish, whereby starch build-up has been prevented, and the clean article dries in about substantially the same time as a clean article that has not been subjected to the superior rinse aid composition of this invention but has been subjected to a commercially available rinse aid composition.

[0052] As to the dishwashers, for example, that are used with the method of preventing starch build-up in this invention, such dishwashers include those which are made commercially available from manufacturers including KitchenAid, Bendix Appliances, Electrolux, Meiko, Hobart, Winterhalter, Equator Appliance, Frigidaire, Asko USA and the like.

[0053] The following examples are provided for illustrative purposes, and are not intended as a restriction on the scope of the invention. Thus, it is obvious that various changes may be made to the specific embodiments of this invention without departing from its spirit. Accordingly, the invention is not to be limited to the precise embodiments shown and described, but only as indicated in the following claims.

Example I

[0054] A first vessel was charged with 500 ml of water and 50 g of commercially available crystalline potato starch. The contents were stirred at ambient temperature to produce a potato starch suspension. A second vessel was charged with 5 grams of Remazol brilliant blue dye (commercially available from Aldrich) and 500 ml of water. The contents were stirred at ambient temperature to produce a dye solution. The dye solution was added to the potato starch suspension to produce a starch-dye solution which was subsequently stirred and heated to 50°C. The starch-dye solution was maintained at 50°C for about 45 minutes, during which 100 grams of sodium sulfate were added in parts (about 4 addi-

tions). To the resulting mixture, a solution having 50 ml of water and 5 grams of tri-basic sodium phosphate was added wherein the resulting final mixture was stirred for 75 minutes while maintaining the temperature at 50°C. After stirring, the final mixture was filtered and the filtrate was discarded. The resulting solid was resuspended in water and refiltered. The washing was repeated until the filtrate obtained was colorless. The resulting final solid was washed with methanol to remove any residual water. The resulting washed final solid was about 50 grams of azure starch as described in this invention (crystalline potato starch with dye covalently bonded to its backbone and having an absorbance of 0.345 at 596 nm). This experiment was performed in a manner very similar to the one described in New Method for the Determination of α-Amylase, Experimentia 23:805, Rinperknecht, H. Wilding, P., and Berk, J. (1967).

Glass slides (about 5.7 cm²) were washed, dried and weighed. A vessel was charged with 120 mLs of water [0055] which was preheated to 80°C and 2.0 grams of azure starch as prepared above. The resulting mixture was stirred and maintained at 80°C for about 15 minutes, after which the resulting product was a thick gel. The starch gel was divided into 40 gram portions that were each charged with 120 mg of surfactant (see Table 1 below for the list of surfactants tested), identical to those used in the superior rinse aid compositions of this invention. The resulting surfactant-gel mixture was then evenly distributed, in 5 mL portions, onto one side of the glass slides with a pipette. The coated slides were dried overnight at ambient temperature, resulting in slides having dry retrograded azure starch gel on one side amounting to about 80-85 milligrams of substance.

About 200 mL of detergent wash (see Table II below for the wash solution formulation) that was added to a 250 mL jacketed beaker. The beaker was connected to a water circulating bath and placed on a magnetic stir hot plate. The detergent wash was stirred, via a stir bar, and maintained at a constant temperature of about 60°C.

[0057] Three slides having dry retrograded azure starch (as prepared above) were submerged upright in the jacketed beaker with the starch containing sides of the slide facing inward. A compound capable of degrading starch (Termamyl 300L, commercially available from Novo) was dosed into the detergent wash in the beaker so that the concentration of starch degrading material was maintained at about 40 ppm. The degradation of azure starch on the slides was monitored by spectrophotometric analysis of the detergent wash at 30 second intervals over a thirty minute time period. As the azure starch degraded, soluble fragments of starch containing dye were liberated into the detergent wash. The colored detergent wash was circulated through a flow cell with a 1 cm path length via a Hewlett Packard peristaltic pump (No. 89052) set at a flow rate of 50 mL per minute. The pumps inlet tube (about 2mm) was fitted with a 45 micron frit to prevent the circulation of any insolube starch fragments into the flow cell. Absorbance was measured at 596 nm using a Hewlett Packard 8453 photodiode array spectrophotometer. The absorbance values increased as the colored detergent wash darkened, indicating that more of the azure starch degraded. All data obtained was analyzed with Hewlett Packard UV-Vis Chemstation software and is set forth in Table III.

Table I

35	Rinse Aid Surfactants*			
	1.	1-decanol sulfate	12.	sodium dodecyl
	2.	2-decanol lactobionamide	13.	C ₁₆₋₁₈
10	3.	dodecanol	14.	C ₁₂ lactobionamde
	4.	tetradecanol	15.	C ₁₃ (EO) ₈ -C ₄ H ₉
	5.	hexadecanol	16.	C ₁₈ (EO) ₈ -C ₄ H ₉
	6.	C12-(EO) ₂	17.	C ₁₂₋₁₅ (EO) ₅ (PO) ₅
5	7.	C12-(EO) ₄	18.	C ₁₂ -15 (EO) ₉ (PO) ₅
	8.	C12-(EO) ₆	19.	C ₁₂₋₁₅ (EO) ₉ (BO) ₁₋₂
	9.	C12-(EO) ₈	20.	C ₁₂₋₁₅ (EO) ₃ (PO) ₅ and
0	10.	C12-15 linear alkyl ethoxy sulfonate		C ₁₂₋₁₅ (EO) ₉ (BO) ₁₋₂ [1:1 ratio]
	11.	C12 alkylbenzene sulfonate	21.	C ₁₂₋₁₅ (EO) ₃ (PO) ₅ and
				C ₁₂₋₁₅ (EO) ₅ (PO) ₅ [1:2 ratio, respectively]
			22.	Control, no surfactant used

^{*}The surfactants are commercially available or made by the following: Nos. 6-8, Nikko Chemical; Nos. 9-10, Stepan; No. 11, Aldrich; Nos. 12-13, Unilever; Nos. 14-15 Henkel; Nos. 16-17, Uniqema; No. 18, BASF.

Table II**

Detergent Wash

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5	Reagent	Weight Percent		
	Nitrilotriacetic acid (40%)	70%		
	Potassium silicate	12.5%		
10	Potassium hydroxide (50%)	5.6%		
	Sodium sulfate	2.0%		
	Water	Balance		

**The reagents were added to a mixing vessel and stirred at ambient temperature. Nitrilotriacetic acid at 40% means 40% nitrilotriacetic acid and 60% water and potassium hydroxide at 50% means 50% potassium hydroxide and 50% water.

Table III

Rinse Aid Surfactant	Absorbance	%Starch degradation***
No. from Table 1		
1	0.31313	90.84
2	0.32207	93.43
3	0.31392	91.07
4	0.28647	83.10
5	0.22655	65.72
6	0.23431	67.97
7	0.1894	54.94
8	0.1759	51.03
9	0.1631	47.31
10	0.31551	91.53
11	0.47965	139.14
12	0.29106	84.43
13	0.26485	76.86
14	0.26088	75.68
15	0.21183	61.45
16	0.37681	109.31
17	0.33231	96.40
18	0.34098	98.92
19	0.25747	74.69
20	0.19577	56.79
21	0.32603	94.58
22	0.34472	100.00

^{***}Percent starch degradation calculated via a ratio using the control absorbance (no surfactant) to mean 100.00% degradation (i.e., % starch degradation = As/Ai • 100).

Example 2

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[0058] A mixing vessel was charged with deionized water and a 4:1 calcium:magnesium mixture to produce water having a hardness of 150 ppm expressed as CaCO₃. A jacketed beaker was charged with 100 grams of the hard water, and a water temperature of about 95°C was maintained. To the water was added a potato starch suspension prepared by adding 15 grams of potato starch (commercially available from Aldrich) to 35 mL of water at about 5°C. To 100 grams of the resulting thick gel were added 50 mL of cold (about 5°C) water. The resulting mixture was blended with a commercially available blender set on liquefy for about 3 minutes, producing the potato starch soil used in the following experiments.

[0059] Ceramic tiles (about 5.7 cm^2) were washed with water and dried. Potato starch soil (1 gram), as prepared above, was uniformly applied to the tiles with a brush. The tiles were air dried at room temperature for 15 minutes, then baked at 71° C for 15 minutes, producing soiled tiles.

[0060] A simulated multi-tank dishwashing machine having a wash tank and a rinse tank was set up. The wash tank was maintained at 65°C and charged with buffer (1.42g/L) and made from potassium silicate (12.5%), KOH (50%) (balance water) to maintain a detergent wash pH of about 10. The detergent wash was dosed with builder (0.56 g/L, commercially available from BASF and sold under the name Sokalan CP7), and Termamyl 300L (enough to produce a 40 ppm solution). The detergent wash was also dosed with 0.0375 g/L surfactant (or 0.25 g/L rinse aid having 15% sur-

factant) (as described in Table IV) in a counter-flow manner to simulate actual dishwashing conditions. The rinse tank was charged with the identical rinse aid surfactant that was dosed into the detergent wash in the form of a 0.0375 g/L water solution at about 70°C. Six (6) soiled tiles (as prepared above) were washed in the detergent wash for 3 minutes, and then rinsed in the rinse tank for 30 seconds. The tiles were then air dried and the entire process was repeated for a total of three cycles (including soiling) to produce washed tiles subjected to rinse aid composition.

[0061] The reflectance of the washed tiles was measured using a Gardner Reflectometer (Model No. 2000) set at 460*nm (UV filter). The washed tiles were uniformly submerged in an iodine solution (containing 1.5% by weight potassium iodide and 0.2% by weight iodine, balance water) for a few seconds, gently rinsed with deionized water, and allowed to air dry for about 15 minutes. The starch build-up on the tiles was recorded as a % Δ R (percent change in reflectance) which is determined by taking the difference in the reflectance of the washed tile and a clean tile, divided by the difference in the reflectance of a soiled, unwashed tile and a clean tile. The reflectance was measured at the center and four corners of each tile and the values from the six tiles were averaged. The % Δ R values are set forth in Table IV.

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Table IV

Surfactant No.	%∆R
11	2
13	23
14	15
19	32
20	47
21	23
22	12

[0062] Visual examinations of articles subjected to the rinse aid compositions of this invention are consistent with the data produced by these experiments, whereby the data indicates that a superior rinse aid composition that does not inhibit starch degradation in a cleaning system exists when a rinse aid composition is formulated with surfactants that result in absorbance values, %ΔR values or both, as described above.

[0063] Moreover, visual examinations confirm that the superior rinse aid compositions of this invention do not interfere with the drying time of the washed articles since all articles subjected to the rinse aid composition of this invention dried in substantially the same time as normally observed when conventional rinse aid compositions that do not prevent starch buildup are used.

Claims

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- 1. A rinse aid composition comprising at least one surfactant selected from the group consisting of a nonionic and anionic surfactant, the rinse aid composition, when contacted with gelled azure starch that is subsequently retrograded and suspended in a detergent wash having a compound capable of causing starch degradation, does not prevent at least about 75% degradation of the suspended azure starch present in the detergent wash as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled form, was not contacted with the rinse aid composition, or the rinse aid composition, when contacted with a washed ceramic tile originally and uniformly soiled with potato starch to display a % ΔR of more than about 24 as determined by monitoring reflectance at 460 nm of a ceramic tile wherein the ceramic tile:
 - (a) is about 5.7 cm^2 ;
 - (b) is, on three occasions, uniformly coated with about 1.0g of potato starch, air dried, washed for about three minutes in a detergent wash at about 65°C and rinsed for about 30 seconds with the rinse aid composition, said detergent wash comprising enough starch degrading material to yield, in no more than about three minutes, a ceramic tile displaying a % ΔR of about 5 wherein the ceramic tile displaying a % ΔR of about 5.7 cm², is, on three occasions uniformly coated with about 1.0 gram of potato starch, washed for about three minutes in the detergent wash and not subjected to the rinse aid composition;

(c) is submerged, for about 5 seconds, in a solution comprising about 1.5% by weight potassium iodide and about 0.2% by weight iodine, rinsed with deionized water and air dried for about 15 minutes,

, or both

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wherein the rinse aid composition prevents starch build-up.

- 2. The rinse aid composition in accordance with claim 1 wherein the rinse aid does not prevent at least about 85% degradation of the suspended azure starch present in the detergent wash as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled from, was not contacted with the rinse aid composition.
- 3. The rinse aid composition in accordance with claim 1 wherein the rinse aid does not prevent at least about 90% degradation of the suspended azure starch present in the detergent wash as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled from, was not contacted with the rinse aid composition.
- **4.** The rinse aid composition in accordance with claim 1 wherein the surfactant is selected from the group consisting of a nonionic and anionic surfactant.
- **5.** The rinse aid composition in accordance with claim 1 wherein the surfactant is nonionic and comprises at least one member selected from the group consisting of:

$$R = \begin{bmatrix} R & R^{1} \\ C & C \\ R & R^{1} \end{bmatrix}_{p} O \begin{pmatrix} R^{2} & R^{2} \\ C & C \\ R^{2} & R^{2} \end{pmatrix}_{q} OR^{3}$$
(I)

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R C(R8)2OH
OH R OH
R OH
n

wherein

- a) each R is independently a hydrogen, C₁ alkyl, hydroxy or alkoxy;
 - b) each R¹ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
 - c) each R² is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
 - d) each R^3 is independently a hydrogen, C_1 - C_{15} alkyl, aryl, C_{1-4} halocarbon, hydroxy or alkoxy;
 - e) p is an integer from about 1 to about 20, preferably about 6 to about 20, and q is an integer from about 0 to about 20, preferably about 6 to about 20, and each t is independently an integer from about 1-5;

(IV)

- f) each R⁴ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- g) R^5 is a C_1 - C_{15} alkyl or aryl;
- h) each R⁶ is independently a hydrogen, C₁-C₁₅ alkyl, aryl hydroxy or alkoxy;
- i) each R⁷ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- j) each R^8 is independently a hydrogen, $C_{1\text{--}4}$ alkyl, $C_{1\text{--}4}$ halocarbon, hydroxy or alkoxy;
- k) each R⁹ is independently a hydrogen, C₁₋₂₀ alkyl, aryl or C₁₋₄ halocarbon;
- I) n is an integer from about 2 to about 40, and
- m) w is an integer from about 0 to about 3.

6. The rinse aid composition in accordance with claim 1 wherein the surfactant is anionic and comprises at least one member selected from the group consisting of:

$$R = \begin{pmatrix} R^{10} \\ C \\ R^{10} \\ C \\ R^{10} \\ C \end{pmatrix} - SO_3 X^{+}$$
(VII)

wherein each Ar is independently a monocyclic or polycyclic aromatic radical and each x^+ is an alkali metal, alkaline earth metal or NH_4^+ , and R^{10} is independently a hydrogen, C_1 - C_{15} alkyl or an aryl, and r is an integer from about 2 to about 8.

- 7. The rinse aid composition in accordance with claim 6 wherein the rinse aid composition comprises a first surfactant represented by structural formula I wherein each R is hydrogen, R¹ is hydrogen, p is an integer from about 11 to about 14, t is 1, q is 8 with a block of 3 ethylene oxide units and a block of 5 propylene oxide units and R³ is a hydrogen, and a second surfactant represented by formula I wherein each R is hydrogen, R¹ is hydrogen, p is an integer from about 11 to about 14, t is 1, q is 10 with a block of 5 ethylene oxide units and a block of 5 propylene oxide units and R³ is hydrogen.
- **8.** The rinse aid composition in accordance with claim 7 wherein the rinse aid composition comprises about 25% to about 100% by weight more of the second surfactant, based on total weight of the first and second surfactant in the rinse aid composition.
 - **9.** A cleaning system comprising:

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A. a rinse aid composition comprising at least one surfactant selected from the group consisting of a nonionic and anionic surfactant, the rinse aid composition, when contacted with gelled azure starch that is subsequently retrograded and suspended in a detergent wash having a compound capable of causing starch degradation, does not prevent at least about 75% degradation of the suspended azure starch present in the detergent wash

as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled form, was not contacted with the rinse aid composition, or the rinse aid composition, when contacted with a washed ceramic tile originally and uniformly soiled with potato starch, does not cause the washed ceramic tile originally and uniformly soiled with potato starch to display a % ΔR of more than about 24 as determined by monitoring reflectance at 460 nm of a ceramic tile wherein the ceramic tile:

(a) is about 5.7 cm^2 ;

(b) is, on three occasions, uniformly coated with about 1.0g of potato starch, air dried, washed for about three minutes in a detergent wash at about 65°C and rinsed for about 30 seconds with the rinse aid composition, said detergent wash comprising enough starch degrading material to yield, in no more than about three minutes, a ceramic tile displaying a % Δ R of about 5 wherein the ceramic tile displaying a % Δ R of about 5 is about 5.7 cm², is, on three occasions uniformly coated with about 1.0 gram of potato starch, washed for about three minutes in the detergent wash and not subjected to the rinse aid composition; (c) is submerged, for about 5 seconds, in a solution comprising about 1.5% by weight potassium iodide

and about 0.2% by weight iodine, rinsed with deionized water and air dried for about 15 minutes,

or both,

wherein the rinse aid composition prevents starch build-up,

and

B. a detergent wash.

- 25 10. The cleaning system in accordance with claim 9 wherein the cleaning system is a dishwashing system.
 - **11.** The cleaning system in accordance with claim 9 wherein the surfactant is selected from the group consisting of a nonionic and anionic surfactant.
- 30 **12.** The cleaning system in accordance with claim 9 wherein the surfactant is nonionic and comprises at least one member selected from the group consisting of:

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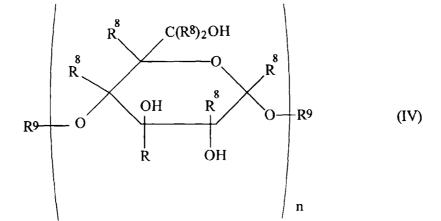
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$$R = \begin{bmatrix} R & R^{1} & R^{2} & R^{2} \\ C & C & C \\ R & R^{2} & R^{2} & R^{2} \\ R^{2} & R^{2} & R^{2} \\ R^{2} & R^{2} & R^{2} \\ R^{2} & R^{2} & R^$$



wherein

a) each R is independently a hydrogen, C₁ alkyl, hydroxy or alkoxy;

- b) each R¹ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- c) each R² is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- d) each R³ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, C₁₋₄ halocarbon, hydroxy or alkoxy;
- e) p is an integer from about 1 to about 20, preferably about 6 to about 20, and q is an integer from about 0 to about 20, preferably about 6 to about 20, and each t is independently an integer from about 1-5;
- f) each R⁴ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- g) R^5 is a C_1 - C_{15} alkyl or aryl;

- h) each R⁶ is independently a hydrogen, C₁-C₁₅ alkyl, aryl hydroxy or alkoxy; i) each R⁷ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy; j) each R⁸ is independently a hydrogen, C₁₋₄ alkyl, C₁₋₄ halocarbon, hydroxy or alkoxy;
- k) each R^9 is independently a hydrogen, C_{1-20} alkyl, aryl or C_{1-4} halocarbon;
- I) n is an integer from about 2 to about 40, and
- m) w is an integer from about 0 to about 3.
- 13. The cleaning system in accordance with claim 9 wherein the surfactant is anionic and comprises at least one mem-15 ber selected from the group consisting of:

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, and

(VI)

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$$R = \begin{pmatrix} R^{10} \\ C \\ R^{10} \\ R^{10} \end{pmatrix} = O - SO_3 X^{+}$$
 (VII)

wherein each Ar is independently a monocyclic or polycyclic aromatic radical and each X⁺ is an alkali metal, alka-55 line earth metal or NH₄⁺, and each R¹⁰ is independently a hydrogen, C₁-C₁₅ alkyl or an aryl, and r is an integer from about 2 to about 8.

- **14.** The cleaning system in accordance with claim 9 wherein the detergent wash comprises an enzyme, caustic agent, oxidizing agent or catalyst.
- 15. A method for preventing starch build-up on an article being cleaned comprising the steps of:
 - a) cleaning an article; and
 - b) subjecting the article to a rinse aid composition for preventing starch build-up comprising at least one surfactant selected from the group consisting of a nonionic and anionic surfactant, the rinse aid composition, when contacted with gelled azure starch that is subsequently retrograded and suspended in a detergent wash having a compound capable of causing starch degradation, does not prevent at least about 75% degradation of the suspended azure starch present in the detergent wash as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled form, was not contacted with the rinse aid composition , or the rinse aid composition, when contacted with a washed ceramic tile originally and uniformly soiled with potato starch, does not cause the washed ceramic tile originally and uniformly soiled with potato starch to display a % Δ R of more than about 22 as determined by monitoring reflectance at 460 nm of a ceramic tile wherein the ceramic tile:
 - (a) is about 5.7 cm²;
 - (b) is, on three occasions, uniformly coated with about 1.0g of potato starch washed for about three minutes in a detergent wash at about 65°C and rinsed for about 30 seconds with the rinse aid composition, said detergent wash comprising enough starch degrading material to yield, in no more than about three minutes, a ceramic tile displaying a % Δ R of about 5 wherein the ceramic tile displaying a % Δ R of about 5 is about 5.7 cm², is, on three occasions uniformly coated with about 1.0 gram of potato starch, washed for about three minutes in the detergent wash and not subjected to the rinse aid composition;
 - (c) is submerged, for about 5 seconds, in a solution comprising about 1.5% by weight potassium iodide and about 0.2% by weight iodine, rinsed with deionized water and air dried for about 15 minutes,

or both.

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- **16.** The method for preventing starch build-up on an article being cleaned in accordance with claim 15 wherein the article is cleaned and subjected to the rinse aid composition for preventing starch build-up in a dishwasher.
- 17. The method for preventing starch build-up on an article being cleaned in accordance with claim 15 wherein the rinse aid composition does not prevent at least about 85% degradation of the suspended azure starch present in the detergent wash as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled from, was not contacted with the rinse aid composition.
- 18. The method for preventing starch build-up on an article being cleaned in accordance with claim 15 wherein the rinse aid composition does not prevent at least about 90% degradation of the suspended azure starch present in the detergent wash as determined by monitoring color development at 596 nm of the detergent wash which comprises about 1.25 grams per liter of suspended azure starch and enough compound capable of degrading, in no more than about 30 minutes, about 1.25 grams of azure starch that, when in its gelled from, was not contacted with the rinse aid composition.
- **19.** The method for preventing starch build-up on an article being cleaned in accordance with claim 15 wherein the surfactant is selected from the group consisting of a nonionic and cationic surfactant.
- **20.** The method for preventing starch build-up on an article being cleaned in accordance with claim 15 wherein the surfactant is nonionic and comprises at least one member selected from the group consisting of:

wherein 45

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- a) each R is independently a hydrogen, C₁ alkyl, hydroxy or alkoxy;
- b) each R¹ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- c) each R^2 is independently a hydrogen, C_1 - C_{15} alkyl, aryl, hydroxy or alkoxy;
- d) each R³ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, C₁₋₄ halocarbon, hydroxy or alkoxy;
- e) p is an integer from about 1 to about 20, preferably about 6 to about 20, and q is an integer from about 0 to about 20, preferably about 6 to about 20, and each t is independently an integer from about 1-5;
- f) each R⁴ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- g) R^5 is a C_1 - C_{15} alkyl or aryl;
- h) each R⁶ is independently a hydrogen, C₁-C₁₅ alkyl, aryl hydroxy or alkoxy;
- i) each R⁷ is independently a hydrogen, C₁-C₁₅ alkyl, aryl, hydroxy or alkoxy;
- j) each R^8 is independently a hydrogen, C_{1-4} alkyl, C_{1-4} halocarbon, hydroxy or alkoxy; k) each R^9 is independently a hydrogen, C_{1-20} alkyl, aryl or C_{1-4} halocarbon;

- I) n is an integer from about 2 to about 40, and
- m) w is an integer from about 0 to about 3.
- **21.** The method for preventing starch build-up on an article being cleaned in accordance with claim 15 wherein the surfactant is anionic and comprises at least one member selected from the group consisting of:

$$A_{r} - O - A_{r} - R^{10}$$
 $SO_{3} - X^{+} SO_{3} - X^{+}$
(V)

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25 P 10

 $\sum_{p=10}^{303} X$, and (VI)

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 $R = \begin{pmatrix} R^{10} \\ C \\ R^{10} \\ R^{10} \end{pmatrix} O - SO_3 X^+$ (VII)

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wherein each Ar is independently a monocyclic or polycyclic aromatic radical and each x^+ is an alkali metal, alkaline earth metal or NH_4^+ , and R^{10} is independently a hydrogen, C_1 - C_{15} alkyl or an aryl, and r is an integer from about 2 to about 8.

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