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(56) Related Art
US 6 506 261 B1 (Man Victor F) 14 January 2003
WO 2005/040320 A (Ecolab Inc; Man Victor F et al.) 6 May 2005
US 3925262 (Laughlin et al.) 9 December 1975
US 6 350 607 B1 (Cooney, Jr. Edward Matthew) 26 February 2002
US 6258765 B1 (Wei et al.) 10 July 2001
WO 02/02727 A (Ecolab Inc) 10 January 2002
US 2005/0020466 A1 (Man et al.) 27 January 2005.
US 6841527 B2 (Mitra et al.) 11 January 2005
GB 1 590 445 A (Unilever Ltd) 3 June 1981
US 2005/020466 Al (Man Victor F Et al.) 27 January 2005
US 4261868 A (Hora et al) 14 April 1981
US 2003/049832 Al (Tisinger Jess Lind Et al.) 13 March 2003
US 2004/0072715 A1 (Griese et al.)15 April 2004
US 5 449 619 A (GRIFFIN ET AL) 12 September 1995

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(54) Title: STABLE SOLID COMPOSITIONS OF SPORES, BACTERIA, FUNGI OR ENZYME

(57) Abstract: The present invention relates to a stable solid cleaning composition including a borate salt and spores (bacterial or fungal), vegetative bacteria, fungi or enzyme, and to methods of using the composition.

STABLE SOLID COMPOSITIONS OF SPORES, BACTERIA, FUNGI AND/OR ENZYME

Field of the Invention

The present invention relates to a stable solid cleaning composition including a borate salt; and spores (bacterial or fungal), vegetative bacteria, fungi or enzyme, and to methods of using the composition.

Background of the Invention

Spores, bacteria, and fungi play an important role in cleaning compositions, particularly those used for cleaning drains and grease traps. Present cleaning compositions including spores, bacteria, or fungi are typically provided as a "two-part" liquid product, with one container of the biological component and a second container of the chemical cleaners. Mixing the chemical cleaners and the biological components and then storing the mixture is not possible due to adverse effects of the chemicals on the spores, bacteria, or fungi. Many enzyme containing compositions have the same shortcomings.

Solid cleaning compositions can present another set of stability issues. Reactive or unstable materials can be kept apart from one another in a solid, which can increase stability. However, many solids include mixed ingredients and require stabilization of a microbe, spore, or enzyme in the composition. Certain dispensers for solid compositions spray liquid on the solid producing a damp solid and a liquid composition including intermediate or high concentration of the dissolved composition and also (optionally) solid matter. In conventional compositions, the microbe, spore, or enzyme can be unstable in the damp solid or liquid composition. Effective dispensing of a solid composition including a microbe, spore, or enzyme benefits from keeping the microbe, spore, or enzyme stable in the damp solid and liquid compositions produced, for example, in a dispenser.

There remains a need for solid compositions including both chemical cleaners and spores, bacteria, fungi, or enzyme.

Summary of the Invention

The present invention relates to a stable solid cleaning composition including a borate salt and spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme, and to methods of using the composition. In an embodiment, the present solid composition includes borate salt and an effective cleaning amount of spore, bacteria, or fungi. The borate salt can include an alkanol amine borate. The present composition can include solidification agent, surfactant, or both. The present method can include applying to a surface or object to be cleaned an aqueous mixture or solution including a composition according to the present invention. The composition applied can include a stabilized microbial composition or a cleaning composition. The surface or object to be cleaned can include one or more of a floor, a drain, or a floor drain. In an embodiment, the present method can include increasing the coefficient of friction of a surface. In an embodiment, the present invention can include cleaning grout. In an embodiment, the surface or grout is a floor or flooring.

In a first aspect there is provided a solid cleaning composition comprising: spore, bacteria, or fungi; about 5 to about 35 wt-% monoethanolammonium borate, diethanolammonium borate, triethanolammonium borate, or a combination thereof; solidification agent, wherein the solidification agent comprises polyethylene glycol, acid salt or mixture thereof; and surfactant, wherein the solid retains at least 70% initial activity of the spore, bacteria, or fungi, for at least one year.

Detailed Description of the Invention

Definitions

As used herein, microbial preparation refers to a composition including one or more of spores (bacterial or fungal), vegetative bacteria, or fungi, which can be provided in a preservative. As used herein, bacteria preparation refers to a composition including bacterial spores and/or vegetative bacteria, which can be provided in a preservative. The preservative can include, for example, any or a variety of preservative compositions used in commercially supplied preparations of spores (bacterial or fungal), vegetative bacteria, or fungi. Such preservatives can include, for example, chelator, surfactant, buffer, water, or the like. The microbial preparation can, for example, digest or degrade soils such as fat, oil, grease, sugar, protein, carbohydrate, or the like.

As used herein, weight percent (wt-%), percent by weight, % by weight, and the like are synonyms that refer to the concentration of a substance as the weight of that substance divided by the weight of the composition and multiplied by 100.

As used herein, boric acid salt and borate salt are used interchangeably to refer to a salt such as potassium borate, monoethanolamine borate, or another salt obtained by or that can be visualized as being obtained by neutralization of boric acid. The weight percent of a boric acid salt or borate salt in a composition of the present invention can be expressed either as the weight percent of either the negatively charged boron containing ion, e.g. the borate and/or boric acid moieties, or as the weight percent of the entire boric acid salt, e.g. both the negatively charged moiety and the positively charged moiety. Preferably, the weight percent refers to the entire boric acid salt. Weight percents of citric acid salts, or other acid salts, can also be expressed in these ways, preferably with reference to the entire acid salt. As used herein, the term "total boron compound" refers to the sum of borate and boric acid moieties.

As used herein, basic or alkaline pH refers to pH greater than 7, greater than or equal to 8, about 8 to about 9.5, about 8 to about 11, greater than about 9, or about 9 to about 10.5.

As used herein, the terms "flooring" or "floor" refer to any horizontal surface on which a person might walk. Flooring or a floor can be made of an inorganic material, such as ceramic tile or natural stone (e.g., quarry tile), or an organic material, such as an epoxy, a polymer, a rubber, or a resilient material. The flooring or floor can be in any of a variety of environments such as a restaurant (e.g., a fast food restaurant), a food processing and/or preparation establishment, a slaughter house, a packing plant, a shortening production plant, a kitchen, or the like.

As used herein, the phrases "coefficient of friction" and "slip resistance" can be defined with respect to any of a variety of standard publications, such as ASTM Standard D-2047, "Static Coefficient of Friction of Polish Coated Floor Surfaces as Measured by the James

Machine" and a report by ASTM Committee D-21 which indicated that a floor having a coefficient of static friction of not less than 0.5 as measured by this test is recognized as providing a non-hazardous walkway surface. This value is qualified in NBS Technical Note 895 "An Overview of Floor Slip-Resistance, With Annotated Bibliography" by Robert J. Brungraber, wherein it is indicated that the value of 0.5 provides a factor of safety and that most people, taking normal strides, would be unlikely to slip on surfaces for which the value is greater than 0.3-0.35. Other relevant and similar standards include ANSI 1264.2-2001, ASTM C1028-89, ASTM D2047-93, ASTM F1679-00 (which relates to the English XL Tribometer), ASTM Test Method F1677-96, and UL 410 (1992). Each of the standards in this paragraph is incorporated herein by reference.

As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and material 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 employed to make the compositions or carry out the methods; and the like. Whether or not modified by the term "about", the claims include equivalents to the quantities.

Solid Compositions Including A Stabilized Microbial Preparation and/or Enzyme

The present invention relates to a solid composition including a borate salt and spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme. The present solid composition can include, for example, solidification agent and stabilized microbial preparation.

The present solid composition can include, for example, solidification agent and stabilized enzyme preparation. The present solid composition can include, for example, solidification agent, stabilized microbial preparation, and stabilized enzyme preparation (e.g., stabilized microbial and enzyme preparation). The present composition can also include one or more of surfactant or surfactant blend, chelating agent, sodium carbonate, or other ingredients useful for cleaning. The present invention also includes methods of using these compositions.

The present composition can provide advantageous stability of spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme. In an embodiment, the present solid including borate salt can provide advantageous stability of the spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme in the solid composition. For example, the solid can retain acceptable levels (e.g., ≥70% initial activity) of active/living spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme for one year, two years, or longer.

In an embodiment, the present solid including borate salt can be employed in a dispenser that wets at least a portion of the surface of the composition to form a concentrate or intermediate liquid composition. In an embodiment, the present solid including borate salt can provide a concentrate or intermediate liquid composition in which the spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme exhibit advantageous stability compared, for example, to such a composition lacking borate salt. For example, the concentrate or intermediate liquid composition can retain acceptable levels (e.g., ≥70% activity) of active/living spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme for 6 hours, 1 day, 2 days, 4 days, 6 days, or longer. In an embodiment, the present solid including borate salt can provide a concentrate or intermediate liquid and particulate composition in which the spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme exhibit advantageous stability compared, for example, to such a composition lacking borate salt. For example, the concentrate or intermediate liquid and particulate composition can retain acceptable levels (e.g., ≥70% activity) of active/living spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme for 6 hours, 1 day, 2 days, 4 days, 6 days, or longer. In an embodiment, the present solid including borate salt can provide a damp solid composition in which the spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme exhibit advantageous stability compared, for example, to such a composition lacking borate salt. For example, the damp solid composition can retain acceptable levels (e.g., ≥70% activity) of active/living spores (bacterial or fungal), vegetative bacteria, fungi, or enzyme for 6 hours, 1 day, 2 days, 4 days, 6 days, or longer.

The present solid composition can include a stabilized microbial preparation including a borate salt and microbe. The microbe can be in the form of spores (bacterial or fungal), vegetative bacteria, or fungi. The microbial preparation can include, for example, spores or spore blend that can digest or degrade soils such as grease, oils (e.g., vegetable oils or animal fat), protein, carbohydrate, or the like. The microbial preparation can also produce enzymes that aid in the degradation of soils such as grease, oil, fat, protein, carbohydrate, or the like. The borate salt can include any of a variety of salts of boric acid, for example, alkali metal salts or alkanol amine salts. The boric acid salt can provide a source of alkalinity for a solid cleaning composition including the stabilized microbial preparation.

The boric acid salt can provide advantageous stability to the microbial preparation compared to a conventional microbial preparation employed in, for example, cleaning compositions. This stability can be manifest, for example, in the solid composition, in a dampened solid composition in a dispenser, in a liquid form of the composition made directly from the solid composition (e.g., a suspension or solution, a concentrate, an intermediate composition, or an use composition).

In an embodiment, the present stabilized microbial preparation is a component of a cleaning composition. Although not limiting to the present invention, the microbial preparation can be viewed as a source of detersive enzyme in the cleaning composition. Such a cleaning composition can also include additional enzymes, not produced by the microbial preparation *in situ*. The microbial preparation can produce, for example, enzymes such as proteases, lipases, and/or amylases. The composition can also include other added enzymes, such as, for example, proteases, lipases, and/or amylases. Although not limiting to the present invention, the added enzymes can be viewed as providing immediate cleaning upon application of the cleaning composition, and the microbial preparation can be viewed as providing persistent cleaning as the microbes remain on the article being cleaned, even after rinsing.

Most cleaners can only provide soil removal which is actually just moving the soil from one surface or location (e.g., a floor) to another (e.g., a drain). In certain embodiments, cleaning compositions including the present stabilized microbial preparation can provide both soil removal and persistent soil reduction, through persistent enzymatic breakdown of soils. Cleaning compositions including the present stabilized microbial preparations can be used for a variety of purposes, including as a floor cleaner, as a grout cleaner, as a combination floor and drain cleaner and degreaser/grease digester, as a grease digester in grease traps, for effluent and/or wastewater treatment (e.g., reduction of fats, oils, and greases), in municipal waste treatment, as a grease digester in rendering plants, or for black and gray water treatment on cruise ships.

The present solid composition can include a stabilized enzyme preparation including a borate salt and enzyme. The enzyme can be a detersive enzyme. The enzyme preparation can include, for example, enzyme or enzyme blend that can digest or degrade soils such as grease, oils (e.g., vegetable oils or animal fat), protein, carbohydrate, or the like. The borate salt can include any of a variety of salts of boric acid, for example, alkali metal salts or alkanol amine salts. The boric acid salt can provide a source of alkalinity for a cleaning composition including the stabilized enzyme preparation.

The boric acid salt can provide advantageous stability to the enzyme preparation compared to a conventional enzyme preparation employed in, for example, cleaning compositions. This stability can be manifest, for example, in the solid composition, in a dampened solid composition in a dispenser, in a liquid form of the composition made directly from the solid composition (e.g., a suspension or solution, a concentrate, an intermediate composition, or an use composition). In an embodiment, the present stabilized enzyme preparation is a component of a solid cleaning composition.

Solid cleaning compositions including the present stabilized enzyme preparations can be used for a variety of purposes, including as a floor cleaner, as a grout cleaner, as a combination floor and drain cleaner and degreaser/grease digester, as a grease digester in grease traps, for effluent and/or wastewater treatment (e.g., reduction of fats, oils, and greases), in municipal waste treatment, as a grease digester in rendering plants, or for black and gray water treatment on cruise ships.

Although not limiting to the present invention, it is believed that the present stable microbial or enzyme compositions can break down grease or oil on a surface. Breaking down the grease or oil can release other soil stuck in the grease or oil. Accordingly, the present solid composition can clean a surface. In an embodiment, the present invention includes a method including repeating application of the present solid stable microbial or enzyme composition. For example, the present method can include daily application. Application for five to 21 days, or even in certain circumstances 5-14 days, can clean a lightly soiled surface. Application for three to six weeks can clean a heavily soiled surface.

Embodiments of the Present Solid Compositions

In certain embodiments, the compositions of the present invention can be described by the ingredients and amounts listed in the tables below. The ingredients of the stabilized microbial composition and/or the stabilized enzyme composition are not listed in the tables below, but are described herein. The amounts or ranges in these tables can also be modified by about.

Table A - Embodiments of Solid Composition

Ingredient	wt-%	wt-%	wt-%	wt-%
Solidification Agent	10-50	15-30	20-25	23
Stabilized Microbial or Enzyme Composition	1-40	2-20	5-15	9
Surfactant	1-70	2-60	50-55	52
Optional Chelating Agent	1-20	1-15	2-10	5

Table B - Embodiments of Solid Composition

Ingredient	wt-%	wt-%	wt-%	wt-%	wt-%
Solidification Agent	5-50	10-25	15-20	18-19	18
Stabilized Microbial or Enzyme Composition	2-40	20-40	25-35	30	30
Surfactant	0.5-70	35-60	40-55	40-41	52

Table C - Embodiments of Solid Composition

Ingredient	wt-%	wt-%	wt-%
Solidification Agent	20-80	50-70	55-65
Stabilized Microbial or Enzyme Composition	1-35	10-15	13
Surfactant	0.1-70	1-10	2-9

Table D- Embodiments of Solid Composition

Ingredient		wt-%	wt-%	wt-%	wt-%
Solidification Agent	PEG	5-25	10-15	5-10	9
	Acid Salt(s) (e.g., sodium acetate, $MgSO_4$)	5-25	10-20	10-15	14
Stabilized Microbial or Enzyme Composition	Borate	2-30	2-20	2-10	5
	Alkanol Amine	1-10	1-10	2-8	4
	Optional Spore	1-10	1-10	2-8	4
	Enzyme	2-15	2-15	5-10	6
Surfactant	Nonionic	1-25	5-15	5-10	15
	Anionic	1-70	30-50	35-45	41
Chelating Agent	EDTA	0-20	1-15	0-10	5

Table E - Embodiments of Solid Composition

Ingredient		wt-%	wt-%	wt-%	wt-%
Solidification Agent	PEG	10-30	15-20	18	18
Stabilized Microbial or Enzyme Composition	Borate	10-25	15-20	17	18
	Alkanol Amine	1-20	5-10	6	10
	Spore	1-10	2-6	3	4
	Enzyme	1-10	2-6	3	8
Surfactant	Nonionic	10-45	20-30	24	24
	Silicone	1-20	2-10	4	4
	Amphoteric	2-20	5-10	8	8

Table F - Embodiments of Solid Composition

Ingredient		wt-%	wt-%	wt-%
Solidification Agent	Sodium Carbonate	20-70	25-35	30
	Acid Salt(s) (e.g., sodium sulfate)	10-50	20-40	25-35
Stabilized Microbial or Enzyme Composition	Borate	2-20	5-15	10
	Spore	0-10	0-5	
	Enzyme	1-10	1-5	3
Surfactant	Nonionic	0.5-40	1-20	2-9
Builder		20-40	25-35	31
Optional Chelating Agent		0-20	5-10	7

Solidification Agent

The solidification agent in the present compositions participates in maintaining the compositions in a solid form. Although other components of the solid composition may also be solids, the solidification agent can maintain the overall composition including solid and liquid components in a solid form. In an embodiment, the solidification agent can assist the source of alkalinity in maintaining the solid cleaning composition in solid form.

Suitable solidification agents include a solid polyethylene glycol (PEG), a solid EO/PO block copolymer, and the like; an amide, such as stearic monoethanolamide, lauric diethanolamide, an alkylamide, or the like; starches that have been made water-soluble through an acid or alkaline treatment process; celluloses that have been made water-soluble; an inorganic agent, such as, sodium hydroxide (e.g., caustic hydrate), a carbonate-based solidification agent (e.g. an E-form or sodium carbonate), sodium acetate, sodium sulfate, alkali metal phosphates (e.g., STPP, TKPP, and TSPP), silicates, such as sodium silicate and sodium metasilicate, or the like; poly(maleic anhydride/methyl vinyl ether); polymethacrylic acid; urea; high melt alcohol ethoxylate (e.g., C12-C14 alcohol ethoxylate with

12, 14, 16, 18, or 20 mole ethoxylate, C12-15 alcohol ethoxylate with 20 mole ethoxylate, C14-15 alcohol ethoxylate with 13 mole ethoxylate, C6 alcohol ethoxylate with 20 mole ethoxylate, or the like); other generally functional or inert materials with high melting points; various inorganics that impart solidifying properties to a heated composition upon cooling; and the like.

In certain embodiments, the solidification agent includes solid PEG, for example PEG 1500 up to PEG 20,000. In certain embodiments, the PEG includes PEG 1450, PEG 3350, PEG 4500, PEG 8000, PEG 20,000, and the like. Additional suitable solidification agents include EO/PO block copolymers such as those sold under the tradenames Pluronic 108, Pluronic F68; amides such as lauric diethanolamide or cocodiethylene amide; and the like. In certain embodiments, the solidification agent includes a combination of solidification agents, such as combination of PEG and an EO/PO block copolymer (such as a Pluronic) and combination of PEG and an amide (such as lauric diethanol amide or stearic monoethanol amide).

In an embodiment, for more controlled dispensing, the solidification agent is not an extremely water soluble solid, such as urea. In this embodiment, other disfavored solidification agents include other hygroscopic solids.

Boric Acid Salts

The present invention relates to a stable microbial cleaning composition that employs one or more boric acid salts to provide improved stability of the microbial preparation, even at basic pH or in an aqueous concentrate prepared from the solid composition. Suitable boric acid salts can provide alkalinity. Such salts include alkali metal boric acid salts; amine boric acid salts, preferably alkanolamine boric acid salts; and the like; or a combination thereof. In certain embodiments, the boric acid salt includes potassium borate, monoethanolammonium borate, diethanolammonium borate, triethanolammonium borate, and the like, or a combination thereof. In an embodiment, the boric acid salt includes monoethanolamine borate.

The boric acid salt, e.g. potassium or monoethanolamine borate, can be obtained by any of a variety of routes. For example, commercially available boric acid salt, e.g. potassium borate, can be added to the composition. Alternatively, the boric acid salt, e.g. potassium or monoethanolamine borate, can be obtained by neutralizing boric acid with a base, e.g. a potassium containing base such as potassium hydroxide or a base such as monoethanolamine.

In certain embodiments, the boric acid salt is soluble in an aqueous concentrate prepared from the solid composition at concentrations in excess of 5 or 10 wt-%, e.g., in excess of 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 wt-%. In certain embodiments, the boric acid salt can be soluble in an aqueous concentrate prepared from the solid composition at concentrations up to 35 wt-%, e.g., up to 25, 30, or 35 wt-%. In certain embodiments, the boric acid salt can be soluble at 12-35 wt-%, 15-30 wt-%, or 20-25 wt-%, e.g., 20-25 wt-%. The present solid compositions can also include any of the quantities or ranges of boric acid salt modified by the term "about".

In an embodiment, alkanol amine borates, such as monoethanolamine borate, are soluble at concentrations larger than other boric acid salts, particularly sodium borate. Alkanol amine borates, such as monoethanolamine borate, can be employed and soluble in an aqueous concentrate prepared from the solid composition at concentrations listed above, preferably up to about 30 weight percent, preferably about 20 to about 25 weight percent. In an embodiment, this high solubility can be obtained at alkaline pH, such as pH about 9 to about 10.5.

In an embodiment, potassium borate is soluble at concentrations larger than other metal boric acid salts, particularly other alkali metal boric acid salts, particularly sodium borate. Potassium borate can be employed and soluble in an aqueous concentrate prepared from the solid composition at concentrations listed above, preferably up to about 25 weight percent, preferably about 15 to about 25 weight percent. In an embodiment, this high solubility can be obtained at alkaline pH, such as pH about 9 to about 10.5.

The boric acid salt can provide desirable increases in microbial preparation stability at basic pH compared to other buffer systems suitable for maintaining a pH above about 7, above about 8, about 8 to about 11, or about 9 to about 10.5. Maintaining alkaline pH can provide greater cleaning power.

In an embodiment, the present cleaning composition includes spore, bacteria, or fungi; and alkanol amine borate. In an embodiment, the composition can include ingredients that when dissolved as a use composition or concentrate composition provide a composition with pH greater than or equal to 9, e.g., about 9 to about 10.5. In an embodiment, the use or concentrate composition can have pH greater than or equal to 8, e.g., about 8 to about 9.5.

In certain embodiments, the present solid composition includes boric acid salt (e.g., alkanolamine borate, e.g., monoethanolamine borate or sodium borate) at about 2 wt-% to about 10 wt-%, at about 5 to about 35 wt-%, at about 5 wt-% to about 20 wt-%, at about 5 wt-% to about 15 wt-%, about 10 wt-% to about 30 wt-%, at about 10 to about 20 wt-%, or at about 25 wt-% to about 30 wt-%. In certain embodiments, borate salt is present at about 5 wt-%, at about 10 wt-%, at about 15 wt-%, at about 20 wt-%, at about 25 wt-%, or at about 30 wt-% of the composition. The present solid compositions can also include any of the quantities or ranges of monoethanolamine borate not modified by the term "about".

Microbial Preparations

Any of a variety of spores (bacterial or fungal), vegetative bacteria, or fungi can be employed in the present stabilized bacterial compositions. For example, the present solid composition can include any viable microorganism or mixture thereof that can survive the formulation and the intended use environment or that can digest, degrade, or promote the degradation of lipids, proteins, carbohydrates, other organic matter, or the like common to domestic, institutional, and industrial soil or effluent, or the like. Many suitable strains and species are known.

Suitable spores (bacterial or fungal), vegetative bacteria, or fungi include Bacillus, Pseudomonas, Arthrobacter, Enterobacter, Citrobacter, Corynebacter, Nitrobacter, mixtures thereof, or the like; Acinetobacter, Aspergillus, Azospirillum, Burkholderia, Ceriporiopsis, Escherichia, Lactobacillus, Paenebacillus, Paracoccus, Rhodococcus, Syphingomonas, Streptococcus, Thiobacillus, Trichoderma, Xanthomonas, Lactobacillus, Nitrosomonas, Alcaliaens, Klebsiella, mixtures thereof, or the like; mixtures thereof, or the like.

Suitable Bacillus include *Bacillus licheniformis*, *Bacillus subtilis*, *Bacillus polymyxa*, mixtures thereof, or the like; *Bacillus methanolicus*, *Bacillus amyloliquefaciens*, *Bacillus pasteurii*, *Bacillus laevolacticus*, *Bacillus megaterium*, mixtures thereof, or the like; mixtures thereof, or the like. Suitable Pseudomonas include *Pseudomonas aeruginosa*, *Pseudomonas alkanolytica*, *Pseudomonas dentrificans*, mixtures thereof, or the like. Suitable Arthrobacter include *Arthrobacter paraffineus*, *Arthrobacter petroleophagus*, *Arthrobacter rubellus*, Arthrobacter sp., mixtures thereof, or the like. Suitable Enterobacter include *Enterobacter cloacae*, Enterobacter sp., mixtures thereof, or the like. Suitable Citrobacter include *Citrobacter amalonaticus*, *Citrobacter freundi*, mixtures thereof, or the like. Suitable Corynebacterium include *Corynebacterium alkanum*, *Corynebacterium fujiokense*, *Corynebacterium hydrocarbooxydano*, Corynebacterium sp. mixtures thereof, or the like.

Suitable spores (bacterial or fungal), vegetative bacteria, or fungi include those with ATCC accession nos. 21417, 21424, 27811, 39326, 6051a, 21228, 21331, 35854, 10401, 12060, 21551, 21993, 21036, 29260, 21034, 13867, 15590, 21494, 21495, 21908, 962, 15337, 27613, 33241, 25405, 25406, 25407, 29935, 21194, 21496, 21767, 53586, 55406, 55405, 55407, 23842, 23843, 23844, 23845, 6452, 6453, 11859, 23492, mixtures thereof, or the like.

Suitable microorganisms that can be used in the present invention include those disclosed in U.S. Patent Nos. 4,655,794, 5,449,619, and 5,863,882; and U.S. Patent Application Publication Nos. 20020182184, 20030126688, and 20030049832; the disclosures of which are incorporated herein by reference.

Suitable spores (bacterial or fungal), vegetative bacteria, or fungi are commercially available from a variety of sources (e.g., Sybron Chemicals, Inc., Semco Laboratories, Inc., or Novozymes). Tradenames for such products include SPORZYME® 1B, SPORZYME® Ultra Base 2, SPORZYME® EB, SPORZYME® BCC, SPORZYME® WC Wash, SPORZYME® FE, BI-CHEM® MSB, BI-CHEM® Purta Treat, BI-CHEM® BDO, BI-CHEM® SANI-BAC®, BI-CHEM® BIO-SCRUB®, BI-CHEM® GC600L®, BI-CHEM® Bioclean, GREASE GUARD®, or the like.

In an embodiment, the spores (bacterial or fungal), vegetative bacteria, or fungi include strains of Bacillus specifically adapted for high production of extracellular enzymes, particularly proteases, amylases and cellulases. Such strains are common in waste treatment products. This mixture can include *Bacillus licheniformis*, *Bacillus subtilis*, and *Bacillus polymyxa*. By way of further example, *Bacillus pasteurii* can exhibit high levels of lipase production; *Bacillus laevolacticus* can exhibit a faster germination cycle; *Bacillus amyloliquefaciens* can exhibit high levels of protease production.

Suitable concentrations for the spores (bacterial or fungal), vegetative bacteria, or fungi in the formula include about $1x10^3$ to about $1x10^9$ CFU/mL, about $1x10^4$ to $1x10^8$ CFU/mL, about $1x10^5$ CFU/mL to $1x10^7$ CFU/mL, or the like. Commercially available compositions of spores (bacterial or fungal), vegetative bacteria, or fungi can be employed in the present solid compositions at effective cleaning compositions, for example, about 0.5 to about 10 wt-%, about 1 to about 5 (e.g., 4) wt-%, about 2 to about 10 wt-%, about 1 to about 3 wt-%, about 2 wt-%, about 3 wt-%, or about 4 wt-%. The present solid composition can include these amounts or ranges not modified by about.

Enzymes

The present cleaning composition can include one or more enzymes, which can provide desirable activity for removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates; for cleaning, destaining, and presoaks. Although not limiting to the present invention, enzymes suitable for the present cleaning compositions can act by degrading or altering one or more types of soil residues encountered on a surface or textile 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.

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. Preferably the enzyme is a protease, a lipase, an amylase, or a combination thereof.

"Detersive enzyme", as used herein, means an enzyme having a cleaning, destaining or otherwise beneficial effect as a component of a composition for laundry, textiles, warewashing, cleaning-in-place, drains, floors, carpets, medical or dental instruments, meat cutting tools, hard surfaces, personal care, or the like. Suitable detersive enzymes include a hydrolase such as a protease, an amylase, a lipase, or a combination thereof.

Enzymes are normally incorporated into a composition according to the invention in an amount sufficient to yield effective cleaning during a washing or presoaking procedure. An amount effective for cleaning refers to an amount that produces a clean, sanitary, and, preferably, corrosion free appearance to the material cleaned. An amount effective for cleaning also can refer to an amount that produces a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates. Typically such a cleaning effect can be achieved with amounts of enzyme from about 0.1% to about 3% by weight, preferably about 1% to about 3% by weight, of the cleaning composition. Higher active levels may also be desirable in highly concentrated cleaning formulations.

Commercial enzymes, such as alkaline proteases, are obtainable in liquid or dried form, are sold as raw aqueous solutions or in assorted purified, processed and compounded forms, and include about 2% to about 80% by weight active enzyme generally in combination with stabilizers, buffers, cofactors, impurities and inert vehicles. The actual active enzyme content depends upon the method of manufacture and is not critical, assuming the composition has the desired enzymatic activity. The particular enzyme chosen for use in the process and products of this invention depends upon the conditions of final utility, including the physical product form, use pH, use temperature, and soil types to be digested, degraded, or altered. The enzyme can be chosen to provide optimum activity and stability for any given set of utility conditions.

The compositions of the present invention preferably include at least a protease. The composition of the invention has further been found, surprisingly, not only to stabilize protease for a substantially extended shelf life, but also to significantly enhance protease activity toward digesting proteins and enhancing soil removal. Further, enhanced protease activity occurs in the presence of one or more additional enzymes, such as amylase, cellulase, lipase, peroxidase, endoglucanase enzymes and mixtures thereof, preferably lipase or amylase enzymes.

The enzyme can be selected for the type of soil targeted by the cleaning composition or present at the site or surface to be cleaned. Although not limiting to the present invention, it is believed that amylase can be advantageous for cleaning soils containing starch, such as potato, pasta, oatmeal, baby food, gravy, chocolate, or the like. Although not limiting to the present invention, it is believed that protease can be advantageous for cleaning soils containing protein, such as blood, cutaneous scales, mucus, grass, food (e.g., egg, milk, spinach, meat residue, tomato sauce), or the like. Although not limiting to the present invention, it is believed that lipase can be advantageous for cleaning soils containing fat, oil, or wax, such as animal or vegetable fat, oil, or wax (e.g., salad dressing, butter, lard, chocolate, lipstick). Although not limiting to the present invention, it is believed that cellulase can be advantageous for cleaning soils containing cellulose or containing cellulose fibers that serve as attachment points for other soil.

The enzyme can include detersive enzyme. The detersive enzyme can include protease, amylase, lipase, cellulase, peroxidase, gluconase, or mixtures thereof. The detersive enzyme can include alkaline protease, lipase, amylase, or mixtures thereof.

A valuable reference on enzymes 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.

Protease

A protease suitable for the composition of the present invention can be derived from a plant, an animal, or a microorganism. Preferably the protease is derived from a microorganism, such as a yeast, a mold, or a bacterium. Preferred proteases include serine proteases active at alkaline pH, preferably derived from a strain of *Bacillus* such as *Bacillus subtilis* or

Bacillus licheniformis; these preferred proteases include native and recombinant subtilisins. The protease can be purified or a component of a microbial extract, and either wild type or variant (either chemical or recombinant). A preferred protease is neither inhibited by a metal chelating agent (sequestrant) or a thiol poison nor activated by metal ions or reducing agents, has a broad substrate specificity, is inhibited by diisopropylfluorophosphate (DFP), is an endopeptidase, has a molecular weight in the range of about 20,000 to about 40,000, and is active at a pH of about 6 to about 12 and at temperatures in a range from about 20°C to about 80°C.

Examples of proteolytic enzymes which can be employed in the composition of the invention include (with trade names) Savinase®; a protease derived from *Bacillus lentus* type, such as Maxacal®, Opticlean®, Durazym®, and Properase®; a protease derived from *Bacillus licheniformis*, such as Alcalase® and Maxatase®; and a protease derived from *Bacillus amyloliquefaciens*, such as Primase®. Preferred commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, or Esperase® by Novo Industries A/S (Denmark); those sold under the trade names Maxatase®, Maxacal®, or Maxapem® by Gist-Brocades (Netherlands); those sold under the trade names Purafect®, Purafect OX, and Properase by Genencor International; those sold under the trade names Opticlean® or Optimase® by Solvay Enzymes; and the like. A mixture of such proteases can also be used. For example, Purafect® is a preferred alkaline protease (a subtilisin) for use in detergent compositions of this invention having application in lower temperature cleaning programs, from about 30°C to about 65°C; whereas, Esperase® is an alkaline protease of choice for higher temperature detersive solutions, from about 50°C to about 85°C. Suitable detersive proteases are described in patent publications including: GB 1,243,784, WO 9203529 A (enzyme/inhibitor system), WO 9318140 A, and WO 9425583 (recombinant trypsin-like protease) to Novo; WO 9510591 A, WO 9507791 (a protease having decreased adsorption and increased hydrolysis), WO 95/30010, WO 95/30011, WO 95/29979, to Procter & Gamble; WO 95/10615 (*Bacillus amyloliquefaciens* subtilisin) to Genencor International; EP 130,756 A (protease A); EP 303,761 A (protease B); and EP 130,756 A. A variant protease employed in the present solid compositions is preferably at least 80% homologous, preferably having at least 80% sequence identity, with the amino acid sequences of the proteases in these references.

In preferred embodiments of this invention, the amount of commercial alkaline protease present in the composition of the invention ranges from about 0.1% by weight of detersive solution to about 3% by weight, preferably about 1% to about 3% by weight, preferably about 2% by weight, of solution of the commercial enzyme product. Typical commercially available detersive enzymes include about 5-10% of active enzyme.

Whereas establishing the percentage by weight of commercial alkaline protease required is of practical convenience for manufacturing embodiments of the present teaching, variance in commercial protease concentrates and in-situ environmental additive and negative effects upon protease activity require a more discerning analytical technique for protease assay to quantify enzyme activity and establish correlations to soil residue removal performance and to enzyme stability within the preferred embodiment; and, if a concentrate, to use-dilution solutions. The activity of the proteases for use in the present invention are readily expressed in terms of activity units -- more specifically, Kilo-Novo Protease Units (KNPU) which are azocasein assay activity units well known to the art. A more detailed discussion of the azocasein assay procedure can be found in the publication entitled "The Use of Azoalbumin as a Substrate in the Colorimetric Determination of Peptic and Tryptic Activity", Tomarelli, R.M., Charney, J., and Harding, M.L., J. Lab. Clin. Chem. 34, 428 (1949).

In preferred embodiments of the present invention, the activity of proteases present in the use-solution ranges from about 1×10^{-5} KNPU/gm solution to about 4×10^{-3} KNPU/gm solution.

Naturally, mixtures of different proteolytic enzymes may be incorporated into this invention. While various specific enzymes have been described above, it is to be understood that any protease which can confer the desired proteolytic activity to the composition may be used and this embodiment of this invention is not limited in any way by specific choice of proteolytic enzyme.

Amylase

An amylase suitable for the composition of the present invention can be derived from a plant, an animal, or a microorganism. Preferably the amylase is derived from a microorganism, such as a yeast, a mold, or a bacterium. Preferred amylases include those derived from a *Bacillus*, such as *B. licheniformis*, *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*. The amylase can be purified or a component of a microbial extract, and either wild type or variant (either chemical or recombinant), preferably a variant that is more stable under washing or presoak conditions than a wild type amylase.

Examples of amylase enzymes that can be employed in the composition of the invention include those sold under the trade name Rapidase by Gist-Brocades® (Netherlands); those sold under the trade names Termamyl®, Fungamyl® or Duramyl® by Novo; Purastar STL or Purastar OXAM by Genencor; and the like. Preferred commercially available amylase enzymes include the stability enhanced variant amylase sold under the trade name Duramyl® by Novo. A mixture of amylases can also be used.

Amylases suitable for the compositions of the present invention include: α-amylases described in WO 95/26397, PCT/DK96/00056, and GB 1,296,839 to Novo; and stability enhanced amylases described in J. Biol. Chem., 260(11):6518-6521 (1985); WO 9510603 A, WO 9509909 A and WO 9402597 to Novo; references disclosed in WO 9402597; and WO 9418314 to Genencor International. A variant α-amylase employed in the present solid compositions can be at least 80% homologous, preferably having at least 80% sequence identity, with the amino acid sequences of the proteins of these references.

Suitable amylases for use in the compositions of the present invention have enhanced stability compared to certain amylases, such as Termamyl®. Enhanced stability refers to a significant or measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylethylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60 °C.; and/or alkaline stability, e.g., at a pH from about 8 to about 11; each compared to a suitable control amylase, such as Termamyl®. Stability can be measured by methods known to those of skill in the art. Suitable enhanced stability amylases for use in the compositions of the present invention have a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature in a range of 25 °C to 55 °C and at a pH in a range of about 8 to about 10. Amylase activity for such comparisons can be measured by assays known to those of skill in the art and/or commercially available, such as the Phadebas® I-amylase assay.

In an embodiment, the amount of commercial amylase present in the composition of the invention ranges from about 0.1% by weight of detersive solution to about 3% by weight, preferably about 1% to about 3% by weight, preferably about 2 % by weight, of solution of the commercial enzyme product. Typical commercially available detersive enzymes include about 0.25-5% of active amylase.

Whereas establishing the percentage by weight of amylase required is of practical convenience for manufacturing embodiments of the present teaching, variance in commercial amylase concentrates and in-situ environmental additive and negative effects upon amylase activity may require a more discerning analytical technique for amylase assay to quantify enzyme activity and establish correlations to soil residue removal performance and to enzyme stability within the embodiment; and, if a concentrate, to use-dilution solutions. The activity of the amylases for use in the present invention can be expressed in known units or through known amylase assays and/or commercially available assays, such as the Phadebas® α-amylase assay.

Naturally, mixtures of different amylase enzymes can be incorporated into this invention. While various specific enzymes have been described above, it is to be understood that any amylase which can confer the desired amylase activity to the composition can be used and this embodiment of this invention is not limited in any way by specific choice of amylase enzyme.

Cellulases

A cellulase suitable for the composition of the present invention can be derived from a plant, an animal, or a microorganism. The cellulase can be derived from a microorganism, such as a fungus or a bacterium. Suitable cellulases include those derived from a fungus, such as *Humicola insolens*, *Humicola* strain DSM1800, or a cellulase 212-producing fungus belonging to the genus *Aeromonas* and those extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. The cellulase can be purified or a component of an extract, and either wild type or variant (either chemical or recombinant).

Examples of cellulase enzymes that can be employed in the composition of the invention include those sold under the trade names Carezyme® or Celluzyme® by Novo, or Cellulase by Genencor; and the like. A mixture of cellulases can also be used. Suitable cellulases are described in patent documents including: U.S. Pat. No. 4,435,307, GB-A-2.075.028, GB-A-2.095.275, DE-OS-2.247.832, WO 9117243, and WO 9414951 A (stabilized cellulases) to Novo.

In an embodiment, the amount of commercial cellulase present in the composition of the invention ranges from about 0.1% by weight of detersive solution to about 3% by weight, preferably about 1% to about 3% by weight, of solution of the commercial enzyme product. Typical commercially available detersive enzymes include about 5-10 percent of active enzyme.

Whereas establishing the percentage by weight of cellulase required is of practical convenience for manufacturing embodiments of the present teaching, variance in commercial cellulase concentrates and in-situ environmental additive and negative effects upon cellulase activity may require a more discerning analytical technique for cellulase assay to quantify enzyme activity and establish correlations to soil residue removal performance and to enzyme stability within the embodiment; and, if a concentrate, to use-dilution solutions. The activity of the cellulases for use in the present invention can be expressed in known units or through known or commercially available cellulase assays.

Naturally, mixtures of different cellulase enzymes can be incorporated into this invention. While various specific enzymes have been described above, it is to be understood that any cellulase which can confer the desired cellulase activity to the composition can be used and this embodiment of this invention is not limited in any way by specific choice of cellulase enzyme.

Lipases

A lipase suitable for the composition of the present invention can be derived from a plant, an animal, or a microorganism. In an embodiment, the lipase is derived from a microorganism, such as a fungus or a bacterium. Suitable lipases include those derived from a *Pseudomonas*, such as *Pseudomonas stutzeri* ATCC 19.154, or from a *Humicola*, such as *Humicola lanuginosa* (typically produced recombinantly in *Aspergillus oryzae*). The lipase can be purified or a component of an extract, and either wild type or variant (either chemical or recombinant).

Examples of lipase enzymes that can be employed in the composition of the invention include those sold under the trade names Lipase P "Amano" or "Amano-P" by Amano Pharmaceutical Co. Ltd., Nagoya, Japan or under the trade name Lipolase® by Novo, and the like. Other commercially available lipases that can be employed in the present solid compositions include Amano-CES, lipases derived from

Chromobacter viscosum, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., and lipases derived from *Pseudomonas gladioli* or from *Humicola lanuginosa.*

A suitable lipase is sold under the trade name Lipolase® by Novo. Suitable lipases are described in patent documents including: WO 9414951 A (stabilized lipases) to Novo, WO 9205249, RD 94359044, GB 1,372,034, Japanese Patent Application 53,20487, laid open Feb. 24, 1978 to Amano Pharmaceutical Co. Ltd., and EP 341,947.

In an embodiment, the amount of commercial lipase present in the composition of the invention ranges from about 0.1% by weight of detersive solution to about 3% by weight, preferably about 1% to about 3% by weight, of solution of the commercial enzyme product. Typical commercially available detersive enzymes include about 5-10 percent of active enzyme.

Whereas establishing the percentage by weight of lipase required is of practical convenience for manufacturing embodiments of the present teaching, variance in commercial lipase concentrates and in-situ environmental additive and negative effects upon lipase activity may require a more discerning analytical technique for lipase assay to quantify enzyme activity and establish correlations to soil residue removal performance and to enzyme stability within the embodiment; and, if a concentrate, to use-dilution solutions. The activity of the lipases for use in the present invention can be expressed in known units or through known or commercially available lipase assays.

Naturally, mixtures of different lipase enzymes can be incorporated into this invention. While various specific enzymes have been described above, it is to be understood that any lipase which can confer the desired lipase activity to the composition can be used and this embodiment of this invention is not limited in any way by specific choice of lipase enzyme.

Additional Enzymes

Additional enzymes suitable for use in the present solid compositions include a cutinase, a peroxidase, a gluconase, and the like. Suitable cutinase enzymes are described in WO 8809367 A to Genencor. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidases suitable for compositions are disclosed in WO 89099813 A and WO 8909813 A to Novo. Peroxidase enzymes can be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, and the like. Additional enzymes suitable for incorporation into the present solid composition are disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. Pat. No. 3,553,139 to McCarty et al., U.S. Pat. No. 4,101,457 to Place et al., U.S. Pat. No. 4,507,219 to Hughes and U.S. Pat. No. 4,261,868 to Hora et al.

An additional enzyme, such as a cutinase or peroxidase, suitable for the composition of the present invention can be derived from a plant, an animal, or a microorganism. Preferably the enzyme is derived from a microorganism. The enzyme can be purified or a component of an extract, and either wild type or variant (either chemical or recombinant). In preferred embodiments of this invention, the amount of commercial additional enzyme, such as a cutinase or peroxidase, present in the composition of the invention ranges from about 0.1% by weight of detersive solution to about 3% by weight, preferably about 1% to about 3% by weight, of solution of the commercial enzyme product. Typical commercially available detersive enzymes include about 5-10 percent of active enzyme.

Whereas establishing the percentage by weight of additional enzyme, such as a cutinase or peroxidase, required is of practical convenience for manufacturing embodiments of the present teaching, variance in commercial additional enzyme concentrates and in-situ environmental additive and negative effects upon their activity may require a more discerning analytical technique for the enzyme assay to quantify enzyme activity and establish correlations to soil residue removal performance and to enzyme stability within the embodiment; and, if a concentrate, to use-dilution solutions. The activity of the additional enzyme, such as a cutinase or peroxidase, for use in the present invention can be expressed in known units or through known or commercially available assays.

Naturally, mixtures of different additional enzymes can be incorporated into this invention. While various specific enzymes have been described above, it is to be understood that any additional enzyme which can confer the desired enzyme activity to the composition can be used and this embodiment of this invention is not limited in any way by specific choice of enzyme.

Solid Compositions Including Surfactant

The surfactant or surfactant admixture of the present invention can be selected from water soluble or water dispersible nonionic, semi-polar nonionic, anionic, cationic, amphoteric, or zwitterionic surface-active agents; or any combination thereof. The particular surfactant or surfactant mixture chosen for use in the process and products of this invention can depend on the conditions of final utility, including method of manufacture, physical product form, use pH, use temperature, foam control, and soil type. Surfactants incorporated into the cleaning compositions of the present invention are preferably enzyme compatible, not substrates for enzymes in the composition, and not inhibitors or inactivators of the enzyme. For example, when proteases and amylases are employed in the present solid compositions, the surfactant is preferably free of peptide and glycosidic bonds. In addition, certain cationic surfactants are known to decrease enzyme effectiveness.

Generally, the concentration of surfactant or surfactant mixture useful in stabilized compositions of the present invention fall in the range of from about 0.5% to about 40% by weight of the composition, preferably about 2% to about 10%, preferably about 5% to about 8%. These percentages can refer to percentages of the commercially available surfactant composition, which can contain solvents, dyes, odorants, and the like in addition to the actual surfactant. In this case, the percentage of the actual surfactant chemical can be less than the percentages listed. These percentages can refer to the percentage of the actual surfactant chemical.

Anionic Surfactants

Also useful in the present invention are surface active substances which are categorized as anionics because the charge on the hydrophobe is negative; or surfactants in which the hydrophobic section of the molecule carries no charge unless the pH is elevated to neutrality or above (e.g. carboxylic acids). Carboxylate, sulfonate, sulfate and phosphate are the polar (hydrophilic) solubilizing groups found in anionic surfactants. Of the cations (counter ions) associated with these polar groups, sodium, lithium and potassium impart water solubility; ammonium and substituted ammonium ions provide both water and oil solubility; and, calcium, barium, and magnesium promote oil solubility.

Anionics are excellent detersive surfactants and are therefore, favored additions to heavy duty detergent compositions. Generally, however, anionics have high foam profiles which limit their use alone or at high concentration levels in cleaning systems such as CIP circuits that require strict foam control. Further, anionic surface active compounds can impart special chemical or physical properties other than detergency within the composition. Anionics can be employed as gelling agents or as part of a gelling or thickening system. Anionics are excellent solubilizers and can be used for hydrotropic effect and cloud point control.

The majority of large volume commercial anionic surfactants can be subdivided into five major chemical classes and additional sub-groups, which are described in "Surfactant Encyclopedia", Cosmetics & Toiletries, Vol. 104 (2) 71-86 (1989). The first class includes acylamino acids (and salts), such as acylgluamates, acyl peptides, sarcosinates (e.g. N-acyl sarcosinates), taurates (e.g. N-acyl taurates and fatty acid amides of methyl tauride), and the like. The second class includes carboxylic acids (and salts), such as alkanoic acids (and alkanoates), ester carboxylic acids (e.g. alkyl succinates), ether carboxylic acids, and the like. The third class includes phosphoric acid esters and their salts. The fourth class includes sulfonic acids (and salts), such as isethionates (e.g. acyl isethionates), alkylaryl sulfonates, alkyl sulfonates, sulfosuccinates (e.g. monoesters and diesters of sulfosuccinate), and the like. The fifth class includes sulfuric acid esters (and salts), such as alkyl ether sulfates, alkyl sulfates, and the like. Although each of these classes of anionic surfactants can be employed in the present solid compositions, it should be noted that certain of these anionic surfactants may be incompatible with the enzymes. For example, the acyl-amino acids and salts may be incompatible with proteolytic enzymes because of their peptide structure.

Anionic sulfate surfactants suitable for use in the present solid compositions include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5 -C_{17} acyl-N-(C_1 -C_4 alkyl) and -N-(C_1 -C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Examples of suitable synthetic, water soluble anionic detergent compounds include the ammonium and substituted ammonium (such as mono-, di- and triethanolamine) and alkali metal (such as sodium, lithium and potassium) salts of the alkyl mononuclear aromatic sulfonates such as the alkyl benzene sulfonates containing from about 5 to about 18 carbon atoms in the alkyl group in a straight or branched chain, e.g., the salts of alkyl benzene sulfonates or of alkyl toluene, xylene, cumene and phenol sulfonates; alkyl naphthalene sulfonate, diamyl naphthalene sulfonate, and dinonyl naphthalene sulfonate and alkoxylated derivatives.

Anionic carboxylate surfactants suitable for use in the present solid compositions include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps (e.g. alkyl carboxyls). Secondary soap surfactants (e.g. alkyl carboxyl surfactants) useful in the present solid compositions include those which contain a carboxyl unit connected to a secondary carbon. The secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in alkyl-substituted cyclohexyl carboxylates. The secondary soap surfactants typically contain no ether linkages, no ester linkages and no hydroxyl groups. Further, they typically lack nitrogen atoms in the head-group (amphiphilic portion). Suitable secondary soap surfactants typically contain 11-13 total carbon atoms, although more carbons atoms (e.g., up to 16) can be present.

Other anionic detergents suitable for use in the present solid compositions include olefin sulfonates, such as long chain alkene sulfonates, long chain hydroxyalkane sulfonates or mixtures of alkenesulfonates and hydroxyalkane-sulfonates. Also included are the alkyl sulfates, alkyl poly(ethyleneoxy) ether sulfates and aromatic poly(ethyleneoxy) sulfates such as the sulfates or condensation products of ethylene oxide and nonyl phenol (usually having 1 to 6 oxyethylene groups per molecule. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

The particular salts will be suitably selected depending upon the particular formulation and the needs therein.

Further examples of suitable anionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Pat. No. 3,929,678, issued Dec. 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

In an embodiment, the present solid composition includes alkyl or alkyl aryl sulfonates or substituted sulfates and sulfated products. In certain embodiments, the present solid composition includes linear alkane sulfonate, linear alkylbenzene sulfonates, alphaolefin sulfonates, alkyl sulfates, secondary alkane sulfates or sulfonates, or sulfosuccinates.

In certain embodiments, the composition can include about 0.003 to about 35 wt-% anionic surfactant, for example, about 5 to about 30 wt-% anionic surfactant. The anionic surfactant can include linear alkyl benzene sulfonate; alpha olefin sulfonate; alkyl sulfate; secondary alkane sulfonate; sulfosuccinate; or mixtures thereof. The anionic surfactant can include alkanol ammonium alkyl benzene sulfonate. The anionic surfactant can include monoethanol ammonium alkyl benzene sulfonate.

Nonionic Surfactant

Nonionic surfactants useful in the invention are generally characterized by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic, alkyl aromatic or polyoxyalkylene hydrophobic compound with a hydrophilic alkaline oxide moiety which in common practice is ethylene oxide or a polyhydration product thereof, polyethylene glycol. Practically any hydrophobic compound having a hydroxyl, carboxyl, amino, or amido group with a reactive hydrogen atom can be condensed with ethylene oxide, or its polyhydration adducts, or its mixtures with alkoxylenes such as propylene oxide to form a nonionic surface-active agent. The length of the hydrophilic polyoxyalkylene moiety which is condensed with any particular hydrophobic compound can be readily adjusted to yield a water dispersible or water soluble compound having the desired degree of balance between hydrophilic and hydrophobic properties.

In an embodiment, the present cleaning composition includes solidification agent; spore, bacteria or fungus; and boric acid salt, e.g., alkanol amine borate. In certain embodiments, the composition can also include about 0.003 to about 35 wt-% nonionic surfactant, for example, about 5 to about 20 wt-% nonionic surfactant. The nonionic surfactant can include nonionic block copolymer comprising of at least $(EO)_y(PO)_z$, wherein y and z are independently between 2 and 100; C_{6-24} alkyl phenol alkoxylate having 2 to 15 moles of ethylene oxide; C_{6-24} alcohol alkoxylate having 2 to 15 moles of ethylene oxide; alkoxylated amine having 2-20 moles of ethylene oxide; or mixtures thereof.

EOPO Nonionic Surfactant

An example of useful nonionic surfactants used with the silicone surfactants are polyether compounds prepared from ethylene oxide, propylene oxide, in a graft moiety homopolymer or a block or heteric copolymer. Such polyether compounds are known as polyalkylene oxide polymers, polyoxyalkylene polymers, or polyalkylene glycol polymers. Such nonionic surfactants have a molecular weight in the range of about 500 to about 15,000. Certain types of polyoxypropylene-polyoxyethylene glycol polymer nonionic surfactants have been found to be particularly useful. Surfactants including at least one block of a polyoxypropylene and having at least one other block of polyoxyethylene attached to the polyoxypropylene block can be used. Additional blocks of polyoxyethylene or polyoxypropylene can be present in a molecule. These materials having an average molecular weight in the range of about 500 to about 15,000 are commonly available as PLURONIC® manufactured by the BASF Corporation and available under a variety of other trademarks of their chemical suppliers. In addition PLURONIC® R (reverse PLURONIC structure) are also useful in the compositions of the invention. Additionally, alkylene oxide groups used with an alcohol and an alkyl phenol, a fatty acid or other such group can be useful. A useful surfactant can include a capped polyalkoxylated C_{6-24} linear alcohol. The surfactants can be made with polyoxyethylene or polyoxypropylene units and can be capped with common agents forming an ether end group. A useful species of this surfactant is a $(PO)_x$ compound or benzyl ether compound polyethoxylated C_{12-14} linear alcohol; see U.S. Patent No. 3,444,247. Particularly useful polyoxypropylene polyoxyethylene block polymers are those including a center block of polyoxypropylene units and blocks of polyoxyethylene units to each side of the center block.

These copolymers have the formula shown below:

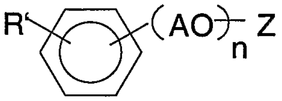
$$(EO)_n - (PO)_m - (EO)_n$$

wherein m is an integer of 21 to 54; n is an integer of 7 to 128. Additional useful block copolymers are block polymers having a center block of polyoxyethylene units and blocks of polyoxypropylene units to each side of the center block. The copolymers have the formula as shown below:

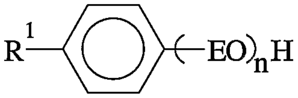
$$(PO)_n - (EO)_m - (PO)_n$$

wherein m is an integer of 14 to 164 and n is an integer of 9 to 22.

One suitable nonionic surfactant for use in the compositions of the invention include an alkyl phenol alkoxylate of the formula:



wherein R' includes a C_{2-24} aliphatic group and AO represents an ethylene oxide group, a propylene oxide group, an heteric mixed EOPO group or a block EO-PO, PO-EO, EOPOEO or POEOPO group, and Z represents H or an (AO), Benzyl or other cap. A suitable nonionic surfactant includes an alkyl phenol ethoxylate of the formula:



wherein R^1 includes a C_{6-18} aliphatic group, preferably a C_{6-12} aliphatic group and n is an integer of about 2 to about 24. A primary example of such a surfactant is a nonyl phenol ethoxylate having 2.5 to 14.5 moles of EO in the ethoxylate group. The ethoxylate group can be capped with a $(PO)_x$ group when x is 2.5 to 12.5 or a benzyl moiety.

Alkoxylated Amines

The present solid compositions can include any of a variety of alkoxylated amines. In an embodiment, the alkoxylated amine has general Formula I: $N(R_1)(R_2)(R_3)(R_4)$, in which at least one of R_1, R_2, or R_3 includes an alkoxylate or ether moiety. R_4 can be hydrogen, straight or branched alkyl, or straight or branched alkyl aryl. The alkoxylated amine can be a primary, secondary, or tertiary amine. In an embodiment, the alkoxylated amine is a tertiary amine. In certain embodiments, each of R_2 and R_3 includes an alkoxylate moiety, e.g., one or more ethoxylate moieties, one or more propoxylate moieties, or combinations thereof, and R_4 is hydrogen. For example, one of R_1, R_2, or R_3 can include an ether moiety and the other two can include one or more ethoxylate moieties, one or more propoxylate moieties, or combinations thereof.

By way of further example, an alkoxylated amine can be represented by general Formulae IIa, IIb, or IIc, respectively:

IIa $R^5\text{--}(PO)_sN\text{--}(EO)_tH$,

IIb $R^5\text{--}(PO)_sN\text{--}(EO)_tH(EO)_uH$, and

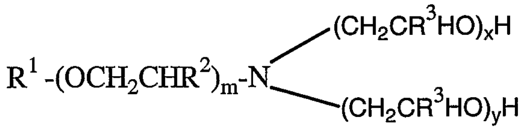
IIc $R^5\text{--}N(EO)_tH$;

in which R^5 can be an alkyl, alkenyl or other aliphatic group, or an alkyl-aryl group of from 8 to 20 or from 12 to 14 carbon atoms, EO is oxyethylene, PO is oxypropylene, s is 1-20, 2-12, or 2 to 5, t is 1-20, 1-10, 2-12, or 2-5, and u is 1-20, 1-10, 2-12, or 2-5. Other variations on the scope of these compounds can be represented by formula IId:

$$R^5\text{--}(PO)_v\text{--}N[(EO)_wH][(EO)_zH]$$

in which R^5 is as defined above, v is 1 to 20 (e.g., 1, 2, 3, or 4 or, in an embodiment, 2), and w and z are independently 1-20, 1-10, 2-12, or 2-5.

In an embodiment, the alkoxylated amine is an ether amine alkoxylate. An ether amine alkoxylate can have Formula III:



$$R^1\text{-}(OCH_2CHR^2)_m\text{-}N\begin{cases}(CH_2CR^3HO)_xH\\(CH_2CR^3HO)_yH\end{cases}$$

In Formula III, R^1 can be a straight or branched alkyl or alkylaryl; R^2 can independently in each occurrence be hydrogen or alkyl from 1 to 6 carbons; R^3 can independently in each occurrence be hydrogen or alkyl of from 1 to 6 carbons; m can average from about 1 to about 20; x and y can each independently average from 1 to about 20; and x+y can average from about 2 to about 40.

In an embodiment, in Formula III, R^1 can be: alkyl of from 8 to 24 carbon atoms, alkylaryl and contain from about 7 to about 30 carbon atoms, or alkylaryl (e.g., alkylaryl disubstituted with alkyl groups); R^2 can contain 1 or 2 carbon atoms or can be hydrogen; R^3 can be hydrogen, alkyl containing 1 or 2 carbons; and x+y can range from about 1 to about 3.

Such ether amine alkoxylates are described in U.S. Patent Nos. 6,060,625 and 6,063,145.

In an embodiment, in Formula III, R^1 can be: alkyl of from 6 to 24 carbon atoms, alkylaryl and contain from about 7 to about 30 carbon atoms, or alkylaryl (e.g., alkylaryl disubstituted with alkyl groups); R^2 can contain 1 or 2 carbon atoms or can be hydrogen; R^3 can be hydrogen, alkyl containing 1 or 2 carbons; and x+y can range from about 1 to about 20.

In an embodiment, in Formula III, m can be 0 to about 20 and x and y can each independently average from 0 to about 20. In certain embodiments, the alkoxy moieties can be capped or terminated with ethylene oxide, propylene oxide, or butylene oxide units.

In an embodiment, in Formula III, R^1 can be C_6-C_{20} alkyl or C_9-C_{13} alkyl, e.g., linear alkyl; R^2 can be CH_3; m can be about 1 to about 10; R^3 can be hydrogen; and x+y can range from about 5 to about 12.

In an embodiment, in Formula III, R^1 can be C_6-C_{14} alkyl or C_7-C_{14} alkyl, e.g., linear alkyl; R^2 can be CH_3; m can be about 1 to about 10; R^3 can be hydrogen; and x+y can range from about 2 to about 12. In an embodiment, such an ether amine alkoxylate can include alkoxylate moieties terminated with propylene oxide or butylene oxide units, which can provide low foam compositions.

In an embodiment, in Formula III, R^1 can be C_6-C_{14} alkyl, e.g., linear alkyl; R^2 can be CH_3; m can be about 1 to about 10; R^3 can be hydrogen; and x+y can range from about 2 to about 20.

In an embodiment, the alkoxylated amine can be a C_{12} to C_{14} propoxy amine ethoxylate in which, in Formula III, R^1 can be C_{12}-C_{14} alkyl, e.g., linear alkyl; R^2 can be CH_3; m can be about 10; R^3 can be hydrogen; x can be about 2.5, and y can be about 2.5.

In an embodiment, the alkoxylated amine can be a C_{12} to C_{14} propoxy amine ethoxylate in which, in Formula III, R^1 can be C_{12}-C_{14}

alkyl, e.g., linear alkyl; R^2 can be CH_3; m can be about 5; R^3 can be hydrogen; x can be about 2.5, and y can be about 2.5.

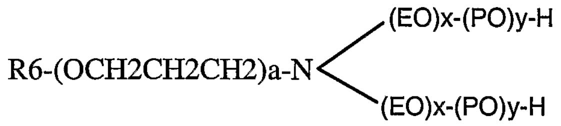
In an embodiment, the alkoxylated amine can be a C_{12} to C_{14} propoxy amine ethoxylate in which, in Formula III, R^1 can be C_{12}-C_{14} alkyl, e.g., linear alkyl; R^2 can be CH_3; m can be about 2; R^3 can be hydrogen; x can be about 2.5, and y can be about 2.5.

In an embodiment, in Formula III, R^1 can be branched C_{10} alkyl; R^2 can be CH_2; m can be 1; R^3 can be hydrogen; and x+y can be about 5. Such an alkoxylated amine can be a tertiary ethoxylated amine known as poly (5) oxyethylene isodecyloxypropylamine.

In an embodiment, the alkoxylated amine can be a secondary ethoxylated amine that can be described by the formula: R-(PO)-N-$(EO)_x$ where x = 1 to 7 moles of ethylene oxide.

In an embodiment the alkoxylated amine can be a diamine that can be described by the formula R-O-CH2CH2CH2N(H)(CH2CH2CH2NH2) in which R is, for example, branched C_{10} alkyl.

In an embodiment, the ether amine alkoxylate of Formula III is an ether amine ethoxylate propoxylate of Formula IV:



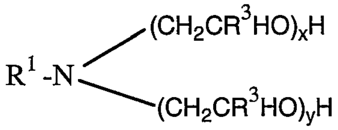
$$\mathrm{R6\text{-}(OCH2CH2CH2)a\text{-}N}\begin{cases}\mathrm{(EO)x\text{-}(PO)y\text{-}H}\\ \mathrm{(EO)x\text{-}(PO)y\text{-}H}\end{cases}$$

In Formula IV, R^6 can be a straight or branched alkyl or alkylaryl; a can average from about 1 to about 20; x and y can each independently average from 0 to about 10; and x+y can average from about 1 to about 20. Such an ether amine alkoxylate can be referred to as an ether amine ethoxylate propoxylate. In certain embodiments, the alkoxy moieties can be capped or terminated with ethylene oxide, propylene oxide, or butylene oxide units.

In an embodiment, the alkoxylated amine can be a C_{12} to C_{14} propoxy amine ethoxylate that can be described by the formula: $R\text{-}(PO)_2N[EO]_{2.5}$ -$H[EO]_{2.5}$-H. In an embodiment, the alkoxylated amine can be a C_{12} to C_{14} propoxy amine ethoxylate that can be described by the formula: $R\text{-}(PO)_{10}N[EO]_{2.5}$ -$H[EO]_{2.5}$-H. In an embodiment, the alkoxylated amine can be a C_{12} to C_{14} propoxy amine ethoxylate that can be described by the formula: $R\text{-}(PO)_5N[EO]_{2.5}\text{-}H[EO]_{2.5}\text{-}H$. In an embodiment, the alkoxylated amine can be a tertiary ethoxylated amine known as poly (5) oxyethylene isodecyloxypropylamine, which has a branched $C_{10}H_{21}$ alkyl group off the ether oxygen. In an embodiment, the alkoxylated amine can be a diamine that can be described by the formula R-O-CH2CH2CH2N(H)(CH2CH2CH2NH2) in which R is branched C_{10} alkyl. In an embodiment, the alkoxylated amine can be a tertiary ethoxylated amine known as iso-(2-hydroxyethyl) isodecyloxypropylamine, which has a branched $C_{10}H_{21}$ alkyl group off the ether oxygen.

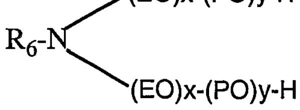
Ether amine alkoxylates are commercially available, for example, under tradenames such as Surfonic (Huntsman Chemical) or Tomah Ether or Ethoxylated Amines.

In an embodiment, the alkoxylated amine is an alkyl amine alkoxylate. A suitable alkyl amine alkoxylate can have Formula V:



In Formula V, R^1 can be a straight or branched alkyl or alkylaryl; R^3 can independently in each occurrence be hydrogen or alkyl of from 1 to 6 carbons; x and y can each independently average from 0 to about 25; and x+y can average from about 1 to about 50. In an embodiment, in Formula V, x and y can each independently average from 0 to about 10; and x+y can average from about 1 to about 20. In an embodiment, the alkoxy moieties can be capped or terminated with ethylene oxide, propylene oxide, or butylene oxide units.

In an embodiment, the alkyl amine alkoxylate of Formula V is an alkyl amine ethoxylate propoxylate of Formula VI:



In Formula VI, R^6 can be a straight or branched alkyl or alkylaryl (e.g., C18 alkyl); x and y can each independently average from 0 to about 25; and x+y can average from about 1 to about 50. In an embodiment, in Formula VI, x and y can each independently average from 0 to about 10 or 20; and x+y can average from about 1 to about 20 or 40. Such an ether amine alkoxylate can be referred to as an amine ethoxylate propoxylate.

One such alkyl amine ethoxylate propoxylate can be described by the chemical names N,N-bis-2(omega-hydroxypolyoxyethylene/polyoxypropylene)ethyl alkylamine or N,N-Bis(polyoxyethylene/propylene) tallowalkylamine, by CAS number 68213-26-3, and/or by chemical formula $C_{64}H_{130}O_{18}$.

Alkyl amine alkoxylates are commercially available, for example, under tradenames such as Armoblen (Akzo Nobel). Armoblen 600 is called an alkylamine ethoxylate propoxylate.

In an embodiment, the alkoxylated amine is an ether amine. Suitable ether amines can have general Formula VII: $N(R_1)(R_2)(R_3)$, in which at least one of R_1, R_2, or R_3 includes an ether moiety. In an embodiment, R_1 includes an ether moiety and R_2, and R_3 are hydrogen. Such an ether amine can have Formula VIII:

$$R_4O(R_5)NH_2$$

In Formula VIII, R_4 can be C_1 to C_{13} arylalkyl or alkyl, straight or branched chain and R_5 can be C_1 to C_6 alkyl, straight or branched chain.

Ether amines are commercially available, for example, from Tomah[3] Products.

Suitable alkoxylated amines can include amines known as ethoxylated amine, propoxylated amine, ethoxylated propoxylated amine, alkoxylated alkyl amine, ethoxylated alkyl amine, propoxylated alkyl amine, ethoxylated propoxylated alkyl amine, ethoxylated propoxylated quaternary ammonium compound, ether amine (primary, secondary, or tertiary), ether amine alkoxylate, ether amine ethoxylate, ether amine propoxylate, alkoxylated ether amine, alkyl ether amine alkoxylate, alkyl propoxyamine alkoxylate, alkylalkoxy ether amine alkoxylate, and the like.

Additional Nonionic Surfactants

Additional useful nonionic surfactants in the present invention include:

Condensation products of one mole of saturated or unsaturated, straight or branched chain carboxylic acid having from about 8 to about 18 carbon atoms with from about 6 to about 50 moles of ethylene oxide. The acid moiety can consist of mixtures of acids in the above defined carbon atoms range or it can consist of an acid having a specific number of carbon atoms within the range. Examples of commercial compounds of this chemistry are available on the market under the trade names Nopalcol® manufactured by Henkel Corporation and Lipopeg® manufactured by Lipo Chemicals, Inc.

In addition to ethoxylated carboxylic acids, commonly called polyethylene glycol esters, other alkanoic acid esters formed by reaction with glycerides, glycerin, and polyhydric (saccharide or sorbitan/sorbitol) alcohols have application in this invention for specialized embodiments, particularly indirect food additive applications. All of these ester moieties have one or more reactive hydrogen sites on their molecule which can undergo further acylation or ethylene oxide (alkoxide) addition to control the hydrophilicity of these substances. Care must be exercised when adding these fatty ester or acylated carbohydrates to compositions of the present invention containing amylase and/or lipase enzymes because of potential incompatibility.

Examples of nonionic low foaming surfactants include nonionic surfactants described above that are modified by "capping" or "end blocking" the terminal hydroxy group or groups (of multi-functional moieties) to reduce foaming by reaction with a small hydrophobic molecule such as propylene oxide, butylene oxide, benzyl chloride; and, short chain fatty acids, alcohols or alkyl halides containing from 1 to about 5 carbon atoms; and mixtures thereof. Also included are reactants such as thionyl chloride which convert terminal hydroxy groups to a chloride group. Such modifications to the terminal hydroxy group may lead to all-block, block-heteric, heteric-block or all-heteric nonionics.

Polyhydroxy fatty acid amide surfactants suitable for use in the present solid compositions include those having the structural formula R^2CONR^1Z in which: R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy group, or a mixture thereof; R_2 is a C_5 - C_{31} hydrocarbyl, which can be straight-chain; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z can be derived from a reducing sugar in a reductive amination reaction; such as a glycityl moiety.

Suitable nonionic alkylpolysaccharide surfactants, particularly for use in the present solid compositions include those disclosed in U.S. Pat. No. 4,565,647, Llenado, issued Jan. 21, 1986. These surfactants include a hydrophobic group containing from about 6 to about 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6-positions on the preceding saccharide units.

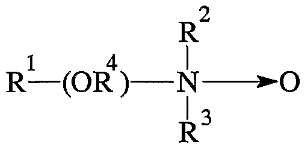
Fatty acid amide surfactants suitable for use the present solid compositions include those having the formula: $R^6CON(R^7)_2$ in which R^6 is an alkyl group containing from 7 to 21 carbon atoms and each R^7 is independently hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, or $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

The treatise Nonionic Surfactants, edited by Schick, M.J., Vol. 1 of the Surfactant Science Series, Marcel Dekker, Inc., New York, 1983 is an excellent reference on the wide variety 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).

Semi-Polar Nonionic Surfactants

The semi-polar type of nonionic surface active agents are another class of nonionic surfactant useful in compositions of the present invention. Generally, semi-polar nonionics are high foamers and foam stabilizers, which can limit their application in CIP systems. However, within compositional embodiments of this invention designed for high foam cleaning methodology, semi-polar nonionics would have immediate utility. The semi-polar nonionic surfactants include the amine oxides, phosphine oxides, sulfoxides and their alkoxylated derivatives.

Amine oxides are tertiary amine oxides corresponding to the general formula:

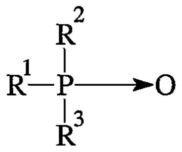


$$R^1\text{—}(OR^4)\text{—}\overset{R^2}{\underset{R^3}{N}}\longrightarrow O$$

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 alkaline or a hydroxyalkylene group containing 2 to 3 carbon atoms; and n ranges from 0 to about 20.

Useful water soluble amine oxide surfactants are selected from the coconut or tallow alkyl di-(lower alkyl) amine oxides, specific examples of which are dodecyldimethylamine oxide, tridecyldimethylamine oxide, etradecyldimethylamine oxide, pentadecyldimethylamine oxide, hexadecyldimethylamine oxide, heptadecyldimethylamine oxide, octadecyldimethylaine oxide, dodecyldipropylamine oxide, tetradecyldipropylamine oxide, hexadecyldipropylamine oxide, tetradecyldibutylamine 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.

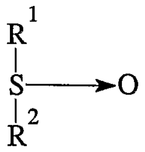
Useful semi-polar nonionic surfactants also include the water soluble phosphine oxides having the following structure:



$$R^1-\overset{\displaystyle R^2}{\underset{\displaystyle R^3}{P}}\longrightarrow O$$

wherein the arrow is a conventional representation of a semi-polar bond; and, R^1 is an alkyl, alkenyl or hydroxyalkyl moiety ranging from 10 to about 24 carbon atoms in chain length; and, R^2 and R^3 are each alkyl moieties separately selected from alkyl or hydroxyalkyl groups containing 1 to 3 carbon atoms.

Examples of useful phosphine oxides include dimethyldecylphosphine oxide, dimethyltetradecylphosphine oxide, methylethyltetradecylphosphone oxide, dimethylhexadecylphosphine oxide, diethyl-2-hydroxyoctyldecylphosphine oxide, bis(2-hydroxyethyl)dodecylphosphine oxide, and bis(hydroxymethyl)tetradecylphosphine oxide. Semi-polar nonionic surfactants useful herein also include the water soluble sulfoxide compounds which have the structure:



$$\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{S}}\longrightarrow O$$

wherein the arrow is a conventional representation of a semi-polar bond; and, R^1 is an alkyl or hydroxyalkyl moiety of about 8 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxyl substituents; and R^2 is an alkyl moiety consisting of alkyl and hydroxyalkyl groups having 1 to 3 carbon atoms.

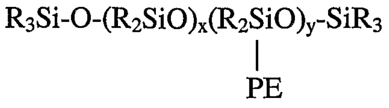
Useful examples of these sulfoxides include dodecyl methyl sulfoxide; 3-hydroxy tridecyl methyl sulfoxide; 3-methoxy tridecyl methyl sulfoxide; and 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Preferred semi-polar nonionic surfactants for the compositions of the invention include dimethyl amine oxides, such as lauryl dimethyl amine oxide, myristyl dimethyl amine oxide, cetyl dimethyl amine oxide, combinations thereof, and the like.

Silicone Surfactant

The silicone surfactant can include a modified dialkyl, e.g., a dimethyl polysiloxane. The polysiloxane hydrophobic group can be modified with one or more pendent hydrophilic polyalkylene oxide group or groups. Such surfactants can provide low surface tension, high wetting, high spreading, antifoaming and excellent stain removal. The silicone surfactants of the invention include a polydialkyl siloxane, e.g., a polydimethyl siloxane to which polyether, typically polyalkylene oxide, groups have been grafted through a hydrosilation reaction. The process results in an alkyl pendent (AP type) copolymer, in which the polyalkylene oxide groups are attached along the siloxane backbone through a series of hydrolytically stable Si-C bond.

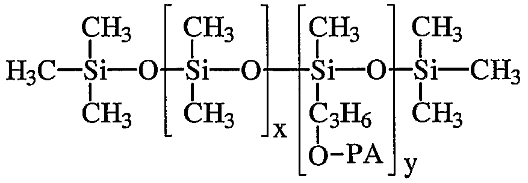
These nonionic substituted poly dialkyl siloxane products have the following generic formula:



$$R_3Si\text{-}O\text{-}(R_2SiO)_x(\underset{\displaystyle PE}{\underset{|}{R_2SiO}})_y\text{-}SiR_3$$

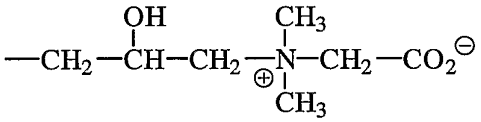
wherein PE represents a nonionic group, e.g., $-CH_2-(CH_2)_p-O-(EO)_m(PO)_n-Z$, with EO representing ethylene oxide, PO representing propylene oxide, x is a number that ranges from about 0 to about 100, y is a number that ranges from about 1 to 100, m, n and p are numbers that range from about 0 to about 50, m+n ≥1 and Z represents hydrogen or R wherein each R independently represents a lower (C_{1-6}) straight or branched alkyl. Such surfactants have a molecular weight (M_n) of about 500 to 20,000.

Other silicone nonionic surfactants have the formula:



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_x-\left[\overset{CH_3}{\underset{C_3H_6-O-PA}{Si}}-O\right]_y-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

$PA = —(C_2H_4O)_a(C_3H_6O)_bR$ or



$$—CH_2—\overset{OH}{CH}—CH_2—\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}—CH_2—CO_2^{\ominus}$$

wherein x represent a number that ranges from about 0 to about 100, y represent a number that ranges from about 1 to about 100, a and b represent numbers that independently range from about 0 to about 60, a+b ≥ 1, and each R is independently H or a lower straight or branched (C_{1-6}) alkyl. A second class of nonionic silicone surfactants is an alkoxy-end-blocked (AEB type) that are less preferred because the Si-O- bond offers limited resistance to hydrolysis under neutral or slightly alkaline conditions, but breaks down quickly in acidic environments.

Suitable surfactants are sold under the SILWET® tradename, the TEGOPREN® trademark or under the ABIL® B trademark. One useful surfactant, SILWET® L77, has the formula:

$$(CH_3)_3Si\text{-}O(CH_3)Si(R^1)O\text{-}Si(CH_3)_3$$

wherein $R^1 = -CH_2CH_2CH_2\text{-}O\text{-}[CH_2CH_2O]_zCH_3$; wherein z is 4 to 16 preferably 4 to 12, most preferably 7-9.

Other useful surfactants include TEGOPREN 5840®, ABIL B-8843®, ABIL B-8852® and ABIL B-8863®.

In certain embodiments, the composition can also include about 0.0005 to about 35 wt-% silicone surfactant, for example, about 1 to about 20 wt-% silicone surfactant. The silicone surfactant can include a silicone backbone and at least 1 pendant alkylene oxide group having from about 2 to 100 moles of alkylene oxide. The pendant alkylene oxide group can include $(EO)_n$ wherein n is 3 to 75.

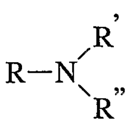
Cationic Surfactants

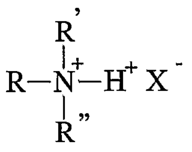
Surface active substances are classified as cationic if the charge on the hydrotrope portion of the molecule is positive. Surfactants in which the hydrotrope carries no charge unless the pH is lowered close to neutrality or lower, but which are then cationic (e.g. alkyl amines), are also included in this group. In theory, cationic surfactants may be synthesized from any combination of elements containing an "onium" structure RnX+Y- and could include compounds other than nitrogen (ammonium) such as phosphorus (phosphonium) and sulfur (sulfonium). In practice, the cationic surfactant field is dominated by nitrogen containing compounds, probably because synthetic routes to nitrogenous cationics are simple and straightforward and give high yields of product, which can make them less expensive.

Cationic surfactants preferably include, more preferably refer to, compounds containing at least one long carbon chain hydrophobic group and at least one positively charged nitrogen. The long carbon chain group may be attached directly to the nitrogen atom by simple substitution; or more preferably indirectly by a bridging functional group or groups in so-called interrupted alkylamines and amido amines. Such functional groups can make the molecule more hydrophilic and/or more water dispersible, more easily water solubilized by co-surfactant mixtures, and/or water soluble. For increased water solubility, additional primary, secondary or tertiary amino groups can be introduced or the amino nitrogen can be quaternized with low molecular weight alkyl groups. Further, the nitrogen can be a part of branched or straight chain moiety of varying degrees of unsaturation or of a saturated or unsaturated heterocyclic ring. In addition, cationic surfactants may contain complex linkages having more than one cationic nitrogen atom.

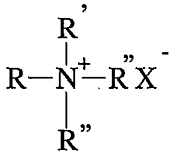
The surfactant compounds classified as amine oxides, amphoterics and zwitterions are themselves typically cationic in near neutral to acidic pH solutions and can overlap surfactant classifications. Polyoxyethylated cationic surfactants generally behave like nonionic surfactants in alkaline solution and like cationic surfactants in acidic solution.

The simplest cationic amines, amine salts and quaternary ammonium compounds can be schematically drawn thus:





$$R-\overset{R'}{\underset{R''}{\overset{|+}{\underset{|}{N}}}}-H^{+}X^{-}$$

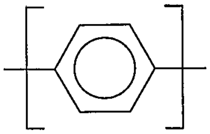


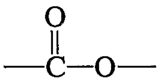
$$R-\overset{R'}{\underset{R''}{\overset{|+}{\underset{|}{N}}}}-R'''X^{-}$$

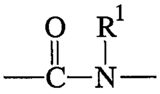
in which, R represents a long alkyl chain, R', R", and R'" may be either long alkyl chains or smaller alkyl or aryl groups or hydrogen and X represents an anion. The amine salts and quaternary ammonium compounds can be useful due to their high degree of water solubility.

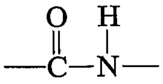
The majority of large volume commercial cationic surfactants can be subdivided into four major classes and additional sub-groups known to those or skill in the art and described in "Surfactant Encyclopedia", Cosmetics & Toiletries, Vol. 104 (2) 86-96 (1989). The first class includes alkylamines and their salts. The second class includes alkyl imidazolines. The third class includes ethoxylated amines. The fourth class includes quaternaries, such as alkylbenzyldimethylammonium salts, alkyl benzene salts, heterocyclic ammonium salts, tetra alkylammonium salts, and the like. Cationic surfactants are known to have a variety of properties that can be beneficial in the present solid compositions. These desirable properties can include detergency in compositions of or below neutral pH, antimicrobial efficacy, thickening or gelling in cooperation with other agents, and the like.

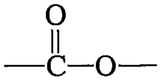
Cationic surfactants useful in the compositions of the present invention include those having the formula $R^{1}{}_{m}R^{2}{}_{x}Y_{L}Z$ wherein each R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to three phenyl or hydroxy groups and optionally interrupted by up to four of the following structures:

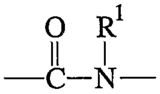


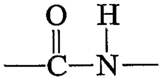

$-\overset{O}{\overset{\|}{C}}-O-$


$-\overset{O}{\overset{\|}{C}}-\overset{R^1}{\overset{|}{N}}-$


$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-$

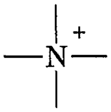

$-\overset{O}{\overset{\|}{C}}-O-$

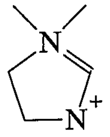

$-\overset{O}{\overset{\|}{C}}-\overset{R^1}{\overset{|}{N}}-$

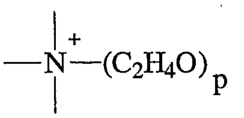

$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-$

or an isomer or mixture of these structures, and which contains from about 8 to 22 carbon atoms. The R^1 groups can additionally contain up to 12 ethoxy groups. m is a number from 1 to 3. Preferably, no more than one R^1 group in a molecule has 16 or more carbon atoms when m is 2 or more than 12 carbon atoms when m is 3. Each R^2 is an alkyl or hydroxyalkyl group containing from 1 to 4 carbon atoms or a benzyl group with no more than one R^2 in a molecule being benzyl, and x is a number from 0 to 11, preferably from 0 to 6. The remainder of any carbon atom positions on the Y group are filled by hydrogens.

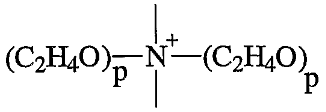
Y is can be a group including, but not limited to:


$-\overset{|}{\underset{|}{N^+}}-$

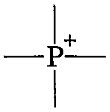


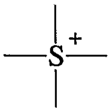

$-\overset{|}{\underset{|}{N^+}}-(C_2H_4O)_p$

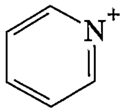
p=about 1 to 12

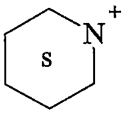

$(C_2H_4O)_p-\overset{|}{\underset{|}{N^+}}-(C_2H_4O)_p$

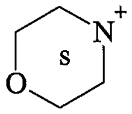
p=about 1 to 12











or a mixture thereof. Preferably, L is 1 or 2, with the Y groups being separated by a moiety selected from R^1 and R^2 analogs (preferably alkylene or alkenylene) having from 1 to about 22 carbon atoms and two free carbon single bonds when L is 2. Z is a water soluble anion, such as a halide, sulfate, methylsulfate, hydroxide, or nitrate anion, particularly preferred being chloride, bromide, iodide, sulfate or methyl sulfate anions, in a number to give electrical neutrality of the cationic component.

<u>Amphoteric Surfactants</u>

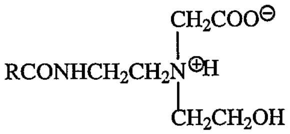
Amphoteric, or ampholytic, surfactants contain both a basic and an acidic hydrophilic group and an organic hydrophobic group. These ionic entities may be any of anionic or cationic groups described herein for other types of surfactants. A basic nitrogen and an acidic carboxylate group are the typical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

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, phosphato, 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). 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.

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.

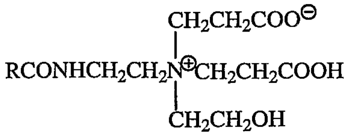
Long chain imidazole derivatives having application in the present invention generally have the general formula:

(MONO)ACETATE



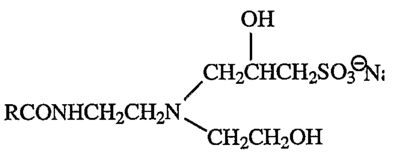
$$\mathrm{RCONHCH_2CH_2}\overset{\mathrm{CH_2COO^{\ominus}}}{\underset{\mathrm{CH_2CH_2OH}}{\mathrm{N}^{\oplus}}}\mathrm{H}$$

(DI)PROPIONATE



$$\mathrm{RCONHCH_2CH_2}\overset{\mathrm{CH_2CH_2COO^{\ominus}}}{\underset{\mathrm{CH_2CH_2OH}}{\mathrm{N}^{\oplus}}}\mathrm{CH_2CH_2COOH}$$

AMPHOTERIC SULFONATE



$$\mathrm{RCONHCH_2CH_2N}\begin{matrix}\diagup\mathrm{CH_2}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2SO_3^{\ominus}N} \\ \diagdown\mathrm{CH_2CH_2OH}\end{matrix}$$

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 solid compositions include for example: Cocoamphopropionate, Cocoamphocarboxy-propionate, Cocoamphoglycinate, Cocoamphocarboxy-glycinate, Cocoamphopropyl-sulfonate, and Cocoamphocarboxy-propionic acid. Preferred amphocarboxylic acids are produced from fatty imidazolines in which the dicarboxylic acid functionality of the amphodicarboxylic acid is diacetic acid and/or dipropionic acid.

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.

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, $RN(C_2H_4COOM)_2$ and $RNHC_2H_4COOM$. In these R is preferably 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.

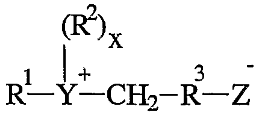
Preferred amphoteric surfactants include those derived from coconut products such as coconut oil or coconut fatty acid. The more preferred of these coconut derived surfactants include as part of their structure an ethylenediamine moiety, an alkanolamide moiety, an amino acid moiety, preferably glycine, or a combination thereof; and an aliphatic substituent of from about 8 to 18 (preferably 12) carbon atoms. Such a surfactant can also be considered an alkyl amphodicarboxylic acid. Disodium cocoampho dipropionate is one most preferred amphoteric surfactant and is commercially available under the tradename Miranol™ FBS from Rhodia Inc., Cranbury, N.J. Another most preferred coconut derived amphoteric surfactant with the chemical name disodium cocoampho diacetate is sold under the tradename Miranol™ C2M-SF Conc., also from Rhodia Inc., Cranbury, N.J.

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

Zwitterionic surfactants can be thought of as a subset of the amphoteric surfactants. 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, sulfate, phosphate, or phosphonate. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

A general formula for these compounds is:

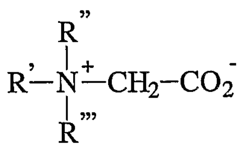


$$R^1-\overset{\overset{\displaystyle (R^2)_x}{|}}{Y^+}-CH_2-R^3-Z^-$$

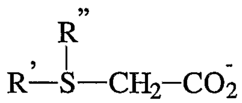
wherein R^1 contains an alkyl, alkenyl, or hydroxyalkyl radical of from 8 to 18 carbon atoms having from 0 to 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^2 is an alkyl or monohydroxy alkyl group containing 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.

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.

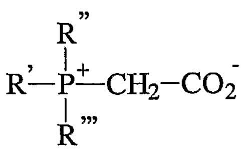
The zwitterionic surfactant suitable for use in the present solid compositions includes a betaine of the general structure:



$R'-\overset{R''}{\underset{R'''}{N^+}}-CH_2-CO_2^-$



$R'-\overset{R''}{S}-CH_2-CO_2^-$



$R'-\overset{R''}{\underset{R'''}{P^+}}-CH_2-CO_2^-$

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} acylmethylamidodiethylammonio-1-carboxybutane; C_{16-18} acylamidodimethylbetaine; C_{12-16} acylamidopentanediethylbetaine; and C_{12-16} acylmethylamidodimethylbetaine.

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.

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).

<u>Surfactant Compositions</u>

The surfactants described hereinabove can be used singly or in combination in the practice and utility of the present invention. In particular, the nonionics and anionics can be used in combination. The semi-polar nonionic, cationic, amphoteric and zwitterionic surfactants can be employed in combination with nonionics or anionics. The above examples are merely specific illustrations of the numerous surfactants which can find application within the scope of this invention. The foregoing organic surfactant compounds can be formulated into any of the several commercially desirable composition forms of this invention having disclosed utility. Said compositions include washing treatments for soiled surfaces in concentrated form which, when dispensed or dissolved in water, properly diluted by a proportionating device, and delivered to the target surfaces as a solution, gel or foam will provide cleaning. Said cleaning treatments consisting of one product; or, involving a two product system wherein proportions of each are utilized. Said product is typically a concentrate of liquid or emulsion.

Additional Ingredients for Solid Stabilized Preparations

The present stabilized microbial preparations and/or cleaning compositions can include any of a variety of ingredients that can be useful for cleaning or other uses. Such ingredients can include hydrotrope, chelating agent, divalent cation, polyol, antimicrobial agent, aesthetic enhancing agent, preservative, or the like.

In certain embodiments, the composition can also include an effective amount of one or more antimicrobials; an effective amount of one or more chelating agents; or mixtures thereof. The composition can include about 0.1 to 30 wt-% of chelating agent. The chelating agent can include small or polymeric compound having carboxyl group, or mixtures thereof.

In certain embodiments, the composition can also include source of calcium ions, polyol, builder, dye, or a combination or mixture thereof.

Sequestrant

The present cleaning composition can include a sequestrant. In general, a sequestrant 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. Some chelating/sequestering agents can also function as a threshold agent when included in an effective amount. 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.

A variety of sequestrants can be used in the present heterogeneous cleaning composition, including, for example, organic phosphonate, aminocarboxylic acid, condensed phosphate, inorganic builder, polymeric polycarboxylate, di- or tricarboxylic acid, mixture thereof, or the like. Such sequestrants and builders are commercially available. In certain embodiments, the present heterogeneous cleaning composition includes about 5 to about 50 wt-%, about 30 to about 50 wt-%, about 10 to about 45 wt-%, or about 20 to about 40 wt-% sequestrant. In certain embodiments, the present heterogeneous cleaning composition includes about 20 wt-%, about 25 wt-%, about 30 wt-%, about 35 wt-%, or about 40 wt-% sequestrant. The composition can include any of these ranges or amounts not modified by about.

Suitable condensed phosphates include sodium and potassium orthophosphate, sodium and potassium pyrophosphate, sodium and potassium tripolyphosphate, sodium hexametaphosphate, for example, tripolyphosphate. In an embodiment, the present heterogeneous cleaning composition includes as a builder, chelator, or sequestrant a condensed phosphate, such as sodium tripolyphosphate.

Polycarboxylates suitable for use as sequestrants include, for example, polyacrylic acid, maleic/olefin copolymer, acrylic/maleic copolymer, polymethacrylic acid, acrylic acid-methacrylic acid copolymers, hydrolyzed polyacrylamide, hydrolyzed polymethacrylamide, hydrolyzed polyamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, hydrolyzed polymethacrylonitrile, hydrolyzed acrylonitrile-methacrylonitrile copolymers, polymaleic acid, polyfumaric acid, copolymers of acrylic and itaconic acid, and the like. In an embodiment, the polycarboxylate includes polyacrylate.

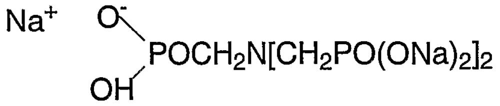
Suitable di- or tricarboxylic acids include oxalic acid, citric acid, or salts thereof. In an embodiment, oxalic acid can be employed for reducing levels of iron in the use composition or removing iron soil from the article being cleaned. For example, oxalic acid can be part of an iron control sour or iron remover.

In an embodiment, the present heterogeneous cleaning composition includes as sequestrant or builder condensed phosphate and polyacrylate, or another polymer, for example, sodium tripolyphosphate and polyacrylate.

The builder can include an organic phosphonate, such as an organic-phosphonic acid and alkali metal salts thereof. Some examples of suitable organic phosphonates include:

1-hydroxyethane-1,1-diphosphonic acid: $CH_3C(OH)[PO(OH)_2]_2$;
aminotri(methylenephosphonic acid): $N[CH_2PO(OH)_2]_3$;

aminotri(methylenephosphonate), sodium salt



$$Na^{+}\ \ {}^{O^{-}}_{OH}\!\!>POCH_2N[CH_2PO(ONa)_2]_2$$

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: $C_9H_{(28-x)}N_3Na_xO_{15}P_5$ (x=7); hexamethylenediamine(tetramethylenephosphonate), potassium salt: $C_{10}H_{(28-x)}N_2K_xO_{12}P_4$ (x=6);

bis(hexamethylene)triamine(pentamethylenephosphonic acid): $(HO_2)POCH_2N[(CH_2)_6N[CH_2PO(OH)_2]_2]_2$; and

phosphorus acid H_3PO_3; and other similar organic phosphonates, and mixtures thereof.

The sequestrant can be or include aminocarboxylic acid type sequestrant. Suitable aminocarboxylic acid type sequestrants include the acids or alkali metal salts thereof, e.g., amino acetates and salts thereof. Some examples include the following:

N-hydroxyethylaminodiacetic acid;

hydroxyethylenediaminetetraacetic acid, nitrilotriacetic acid (NTA);

methylglycinediacetic acid (MGDA);

ethylenediaminetetraacetic acid (EDTA);

N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA);

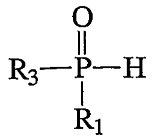
diethylenetriaminepentaacetic acid (DTPA); and

alanine-N,N-diacetic acid;

imidodisuccinic acid;

and the like; and mixtures thereof.

One useful builder/chelating agent or salt thereof includes a polymeric phosphinocarboxylic acid including salts thereof and derivatives thereof. Such materials can be prepared by reacting an unsaturated carboxylic acid monomer such as acrylic acid with a hypophosphorous acid or derivative thereof generally represented by the following formula:



$$R_3-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R_1}{|}}{P}}-H$$

where R_1 is a group OX wherein X is hydrogen or a straight or branched alkyl group containing 1 to 4 carbon atoms; and R_3 is hydrogen, a straight or branched alkyl group of 1 to 8 carbon atoms, a cycloalkyl group of 5 to 12 carbon atoms, a phenyl group, a benzyl group or an -OX group wherein X is hydrogen or a straight or branched alkyl group of 1 to 4 carbon atoms. Salts of the polyphosphinocarboxylic acid can also be employed as noted. One preferred embodiment of such a material is Belsperse® -161.

The sequestrant can be or include a biodegradable sequestrant. Suitable biodegradable sequestrants include methyl glycine diacetic acid or its salts. Such a sequestrant is commercially available, for example, under the tradename Trilon ES.

Enzyme Stabilizing System

The present solid compositions can also include ingredients to stabilize one or more enzymes. For example, the cleaning composition of the invention can include a water-soluble source of calcium and/or magnesium ions. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Compositions, especially liquids, can include from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the listed calcium salts may be used. Further increased levels of calcium and/or magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Stabilizing systems of certain cleaning compositions, for example warewashing compositions, may further include from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during warewashing, can be relatively large; accordingly, enzyme stability to chlorine in-use can be problematic.

Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired.

In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, there is no requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is unacceptably incompatible, as formulated, with other reactive ingredients. In relation to the use of ammonium salts, such salts can be simply admixed with the composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in U.S. Pat. No. 4,652,392, Baginski et al.

Divalent Ion

The cleaning compositions of the invention can contain a divalent ion, such as calcium and magnesium ions, at a level of from 0.05% to 5% by weight, from 0.1% to 1% by weight, or about 0.25% by weight of the composition. In an embodiment, calcium ions can be included in the present solid compositions. The calcium ions can, for example, be added as a chloride, hydroxide, oxide, formate or acetate, or nitrate, preferably chloride, salt.

Polyol

The stabilized microbial preparation or cleaning composition of the invention can also include a polyol. The polyol can, for example, provide additional stability and hydrotrophic properties to the composition. Suitable polyols include glycerin; glycols, such as ethylene glycol, propylene glycol, or hexylene glycol; sorbitol; alkyl polyglycosides; and mixtures thereof. In an embodiment, the polyol includes propylene glycol.

Suitable alkyl polyglycosides for use as polyols according to the invention include those with the formula:

$$(G)_x\text{-O-R}$$

in which G is a moiety derived from reducing saccharide containing 5 or 6 carbon atoms, e.g., pentose or hexose, R is a fatty aliphatic group containing 6 to 20 carbon atoms, and x is the degree of polymerization (DP) of the polyglycoside representing the number of monosaccharide repeating units in the polyglycoside. Preferably, x is about 0.5 to about 10. In an embodiment, R contains 10-16 carbon atoms and x is 0.5 to 3.

In an embodiment, the polyol can be in the form of a polyether. Suitable polyethers include polyethylene glycols. Suitable polyethers include those listed below as solvent or co-solvent.

In certain embodiments, the present solid composition includes about 2 to about 30 wt-% polyol, about 2 to about 10 wt-% polyol, about 5 to about 20 wt-% polyol, about 5 to about 10 wt-% polyol, or about 10 to about 20 wt-% polyol. In certain embodiments, the present stabilized microbial preparations include about 2 to about 40 wt-% polyol, about 2 to about 20 wt-% polyol, about 2 to about 15 wt-% polyol, about 2 to about 10 wt-% polyol, about 3 to about 10 wt-% polyol, about 4 to about 15 wt-% polyol, or about 4 to about 8 wt-% polyol, about 4 wt-% polyol, about 8 wt-% polyol, or about 12 wt-% polyol. The composition can include any of these ranges or amounts not modified by about.

Antimicrobial Agent

In certain embodiments, the present composition can include antimicrobial agent. For example, a composition including an enzyme can include any of a variety of antimicrobial agents compatible with the enzyme and enzyme activity. For example, a composition including a spore can include any of a variety of antimicrobial agents compatible with the spore. The antimicrobial agent can be selected to persist for a shorter time than the spore. After the antimicrobial agent is sufficiently gone, the spore can germinate to form microbes without the microbe being killed or inhibited by the antimicrobial agent. For example, a composition including a microbe can include an antimicrobial agent ineffective against that microbe.

Any of a variety of suitable antimicrobial agents can be employed at effective antimicrobial concentration. Antimicrobial agents include active oxygen compounds (e.g., hydrogen peroxide, percarbonate, perborate, and the like), halogen containing compounds, amine or quaternary ammonium compounds, or the like. Suitable antimicrobial agents include aliphatic amine, ether amine or diamine.

In an embodiment, the present composition can include an effective amount (e.g., antimicrobial amount) of ether amine of Formula 1:

$$R_1\text{-}O\text{-}R_2\text{-}NH_2;$$

of Formula 2:

$$R_1\text{-}O\text{-}R_2\text{-}NH\text{-}R_3\text{-}NH_2;$$

or mixtures thereof. In Formula 1 and Formula 2 (independently) R_1 can be a linear saturated or unsaturated C_6-C_{18} alkyl, R_2 can be a linear or branched C_1-C_8 alkyl, and R_3 can be a linear or branched C_1 -C_8 alkyl. In an embodiment, R_1 is a linear C_{12}-C_{16} alkyl; R_2 is a C_2 -C_6 linear or branched alkyl; and R_3 is a C_2-C_6 linear or branched alkyl. In an embodiment, the present composition includes a linear alkyl ether diamine compound of Formula 2 in which R_1 is C_{12}-C_{16}, R_2 is C_3, and R_3 is C_3. In an embodiment, R1 is either a linear alkyl C_{12}-C_{16} or a mixture of linear alkyl C_{10} -C_{12} and C_{14} -C_{16}. Suitable ether amines are commercially available from Tomah Products Incorporated as PA-19, PA-1618, PA-1816, DA-18, DA-19, DA-1618, DA-1816, and the like.

In an embodiment, the antimicrobial agent can include or be a diamine, such as a diamine acetate. Suitable diamines, shown as the acetates, include those having the formulas:

$$[(R^1)NH(R^2)NH_3\ ]^+\ (CH_3\ COO)^-$$

or

$$[(R^1)NH_2(R^2)NH_3^{++}](CH_3COO)_2^-$$

in which R^1 can be C10-C18 aliphatic group or an ether group having the formula $R^{10}OR^{11}$ in which R^{10} is a C10-C18 aliphatic group and R^{11} is a C1-C5 alkyl group; and R^2 is a C1-C5 alkylene group. Suitable diamine acetates include those in which R^1 is a C10-C18 aliphatic group derived from a fatty acid and R^2 is propylene. The diamine can have a counter ion other than acetate.

Representative examples of useful diamines include N-coco-1,3-propylene diamine, N-oleyl-1,3-propylene diamine, N-tallow-1,3-propylene diamine, and mixtures thereof. Such N-alkyl-1,3-propylene diamines are available from Akzo Chemie America, Armak Chemicals under the trademark Duomeen.

The amount of the amine compound in the composition can be about 0.1 wt-% to 90 wt-%, about 0.25 wt-% to 75 wt-%, or about 0.5 wt-% to 50 wt-%. The amount of the amine compound in use compositions can be about 10 ppm to 10000 ppm, about 20 ppm to 7500 ppm, and about 40 ppm to 5000 ppm.

In an embodiment, the present composition can provide greater than 3 $\log_{10}$ reduction of bacteria within a 5 minute contact time. In an embodiment, the present composition can provide in excess of 5 $\log_{10}$ reduction of microorganisms. This can be advantageous in food preparation and food processing and other areas where triglyceride fats and lipids are soil components.

Acidulants

Acidulants or alkaline agents are used to maintain the appropriate pH for the cleaners of the invention. Careful pH control can enhance cleaning. The acidic component or acidulant used to prepare the cleaners of the invention will include an acid which can be dissolved in the aqueous system of the invention to adjust the pH downward. Preferably, common commercially-available weak inorganic and organic acids can be used in the invention. Useful weak inorganic acids include phosphoric acid and sulfamic acid. Useful weak organic acids include acetic acid, hydroxyacetic acid, citric acid, tartaric acid and the like. Acidulants found useful include organic and inorganic acids such as citric acid, lactic acid, acetic acid, glycolic acid, adipic acid, tartaric acid, succinic acid, propionic acid, maleic acid, alkane sulfonic acids, cycloalkane sulfonic acids, as well as phosphoric acid and the like or mixtures thereof.

Additional Sources of Alkalinity

Alkaline materials that can be used for pH adjustment include both weak and strong alkaline materials. Such materials include strong bases such as sodium hydroxide, potassium hydroxide, alkali metal salts such as sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, sodium sesquicarbonate, sodium borate, potassium borate, sodium phosphate, and potassium phosphate, organic bases such as triethanolamine, tripropanolamine, etc., alkali metal silicates, alkali metal salts generally.

Additional sources of alkalinity can include potassium hydroxides or basic potassium salts such as potassium carbonate, potassium bicarbonate, potassium phosphate, etc.

Dye

The composition of the invention can also include a dye. The dye advantageously provides visibility of the product in a package, dispenser, and/or lines to the composition. A wide variety of dyes are suitable, including Acid Green 25 and Direct Blue 86.

Use Compositions

The compositions and methods of the invention are suitable for removing complex organic or greasy soils and inorganic soils from a variety of substrates. The compositions of the invention can be mixed with or dissolved in water or other liquid medium to form a degreasing aqueous solution.

A use composition can include any of the wt-% amounts of ingredients listed above divided by the amount of dilution, and can be expressed as wt-% or ppm. In particular, the amounts listed above for boric acid salt and microbial component or spore are for solid compositions. For example, a use composition can include any of the wt-% amounts listed above divided independently by 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, or 10000. In an embodiment, the dilution is by a factor of 2 oz of concentrate to 1 gallon of use composition.

Foaming

In an embodiment, the present solid composition can be mixed with diluent to form a use composition that is used in a foamer. Foaming application can be accomplished, for example, using a foam application device such as a tank foamer or an aspirated wall mounted foamer, e.g., employing a foamer nozzle of a trigger sprayer. Foaming application can be accomplished by placing the use composition in a fifteen gallon foam application pressure vessel, such as a fifteen gallon capacity stainless steel pressure vessel with mix propeller. The foaming composition can then be dispensed through a foaming trigger sprayer. A wall mounted foamer can use air to expel foam from a tank or line. In an embodiment, compressed air can be injected into the mixture, then applied to the object through a foam application device such as a tank foamer or an aspirated wall mounted foamer.

Mechanical foaming heads that can be used according to the invention to provide foam generation include those heads that cause air and the foaming composition to mix and create a foamed composition. That is, the mechanical foaming head causes air and the foaming composition to mix in a mixing chamber and then pass through an opening to create a foam.

Suitable mechanical foaming heads that can be used according to the invention include those available from Airspray International, Inc. of Pompano Beach, Florida, and from Zeller Plastik, a division of Crown Cork and Seal Co. Suitable mechanical foaming heads that can be used according to the invention are described in, for example, U.S. Patent No. D-452,822; U.S. Patent No. D-452,653; U.S. Patent No. D-456,260; and U.S. Patent No. 6,053,364. Mechanical foaming heads that can be used according to the invention includes those heads that are actuated or intended to be actuated by application of finger pressure to a trigger that causes the foaming composition and air to mix and create a foam. That is, a person's finger pressure can cause the trigger to depress thereby drawing the foaming composition and air into the head and causing the foaming composition and air to mix and create a foam.

Methods Employing the Present Solid Compositions

In an embodiment, an aqueous dispersion of the present solid composition is directly applied to a heavy soil deposit, permitted to soften and promote soil removal. Once the composition has been permitted to enhance the removability of the soil, the cleaner and removed soil can be readily removed with a rinse step. In an embodiment, the method omits rinsing. That is, an aqueous dispersion of the present solid composition can be applied and the surface is not rinsed. Liquid containing the compositions of the invention including an anionic surfactant can be directly contacted with the hard surface for the removal of organic, oily or greasy soils. Depending on substrate, such a composition can additionally include a chelating agent to have a final formulation including an anionic surfactant and a chelating agent. These compositions can be used on substantially non-corrosive surfaces such as plastics, wood, coated wood, stainless steels, composite materials, fabrics, cement, and others.

In an embodiment, the present method includes a method of cleaning a hard surface. The method can include applying to the surface a cleaning composition including spore, bacteria, or enzyme; borate salt; and anionic surfactant. The method can include applying the composition to a floor, a drain, or a combination thereof.

In an embodiment, the present method includes a method of cleaning a floor. Such a method can include increasing the coefficient of friction of the floor. Such a method can include cleaning the grout of a tile floor. Cleaning grout can include allowing more of its natural color to show. The method includes applying a stabilized spore composition according to the present invention to the floor. In an embodiment, the method does not include (e.g., omits) rinsing. In an embodiment, the present method can include effectively removing from flooring (e.g., tile) a slippery-when-wet film. The method can include cleaning the flooring and increasing its coefficient of friction.

In an embodiment, the present method of cleaning a hard surface can include applying a liquid dispersion of the present solid composition to a bathroom surface, such as a wall, floor, or fixture. The bathroom surface can be a shower wall or surface. The bathroom surface can be a tiled wall. A composition for use on a vertical surface can include a thickener, humectant, or foaming surfactant. Applying the composition to the vertical surface can include foaming the composition. In an embodiment, the present solid composition includes a thickener or humectant, which can assist in retaining the composition on a horizontal or vertical surface. In an embodiment, the present method of cleaning a hard surface can include applying a liquid dispersion of the present solid composition to ware.

In an embodiment, the present method can include applying a liquid dispersion of the present solid composition to a surface that has grease or oil on it. Such surfaces include a floor, a parking lot, a drive through pad, a garage floor, a parking ramp floor, and the like.

In an embodiment, the present method includes spraying or misting a surface with a liquid dispersion of the present solid composition.

In an embodiment, the present method includes applying the stabilized microbial composition to a surface and keeping the surface moist for an extended period, such as one or two hours up to about eight to about 16 hours. Keeping the surface moist can be accomplished by repeated application of the composition, such as by misting. Keeping the surface moist can be accomplished by contacting the surface with a sponge, rag, or mop wet with the composition for an extended period. Keeping the surface moist can be accomplished by applying a persistent stable microbial composition. A persistent stable microbial composition can remain on the surface and keep the surface moist. For example, a thickened composition and certain foamed compositions can remain on the surface and keep the surface moist. Extended presence of the present solid composition can provide more rapid cleaning compared to a composition that dries or evaporates.

The present invention may be better understood with reference to the following examples. These examples are intended to be representative of specific embodiments of the invention, and are not intended as limiting the scope of the invention.

EXAMPLES

Example 1 -- Enzyme Stabilization by Solid Borate Compositions

Compositions according to the present invention were evaluated for stabilization of enzyme. Dispensers for solid cleaning compositions produce a damp solid cleaning composition, a mixture of solid cleaning composition and water, and/or a concentrated solution of dissolved solid cleaning composition. Experimental conditions were created in an attempt to model the damp solids and other mixtures and concentrates produced by dispensers for solid cleaning compositions. The stability of enzyme from a solid cleaning composition was evaluated in these experimental models.

Experiment 1

The components listed in Table 1 were mixed to form a solid cleaning composition. A portion of the solid cleaning composition was mixed with water and allowed to sit Compositions 2-5 were mixed with an equal weight of water. Compositions 6 and 8 were made up to several concentrations. The activity of enzyme in this aqueous mixture was measured at intervals reported in the results. The enzyme was assayed with commercially available reagents and methods.

Table 1 - Solid Compositions Including A Stabilized Microbial or Enzyme Preparation Used in Experiment 1

Composition (wt-%)

Ingredient	1	2	3	4	5	6	7	8	Ex2
Solidification Agent	18	31	19	18	36	9	9	9	9
Sodium Acetate						6.4	6.4	6.4	6.4
Magnesium Sulfate						7.5	7.5	7.5	7.5
Borate	17		18	18		5	5		5
Alkanol Amine	5.8	10	10	10	10	4	4		4
Nonionic Surfactant	24	15	9	9	9	11	11	16	16
Silicone Surfactant	4.1	5	5	5	5				
Anionic Surfactant	16	27	27	27	27	41	37	46	41
Amphoteric Surfactant	8.3								
Chelating Agent						5	5	5	5
Spores	3.3	4	4	4	4		4		
Lipase	3.3	8	8	8	8	6	6	6	6
Water						6	6	6	
$CaCl_2$				0.75	0.75				
Dye		0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Fragrance		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

In these compositions, the solidification agent included PEG 8000, and, in certain compositions sodium acetate and magnesium sulfate. The borate was supplied as boric acid. The alkanol amine was monoethanolamine. In composition 1, the nonionic surfactant was a linear alcohol alkoxylate (e.g., a poly (13) oxyethylene C14-15 alcohol, commercially available from Tomah[3] Products, Inc. under the trade name

Tomadol 45-13) or a linear alcohol ethoxylate (e.g., a C12-C14 alcohol ethoxylate with 9 mol EO, such as that sold under the tradename Surfonic 24-9), plus an amine oxide, e.g. an alkyldimethyl amine oxide, e.g., lauryl dimethyl amine oxide, which is available under the tradename Barlox 12, or an amine oxide available under the tradename Incromine Oxide S. In compositions 2-5, the nonionic surfactant was a linear alcohol alkoxylate (e.g., a poly (13) oxyethylene C14-15 alcohol, commercially available from Tomah[3] Products, Inc. under the trade name Tomadol 45-13). In compositions 6-8, the nonionic surfactant was an alcohol 10-12 ethoxy 6 mole EO and alkyl polyglycoside (supplied as 50% active). The anionic surfactant was sodium alkyl benzene sulfonate flake. The chelating agent was EDTA. The silicone surfactants were those available under the tradenames Abil 8843 and Abil. The amphoteric surfactant was a dicarboxylic coconut sodium salt. The lipase was a commercially available product, as was the spore.

Table 2 -- Lipase Activity After Forming Aqueous Mixtures of Compositions 2-5 (% Control)

	Composition			
Day	2	3	4	5
0	2	76	76	3
2	1	72	70	1
6	0	73	68	0

Table 3 -- Lipase Activity After Forming Aqueous Mixtures of Compositions 6 and 8 (% Control)

Composition	6		8	
Time	0 Hours	24 Hours	0 Hours	24 Hours
1% solid in water	88	10	0	0
10% solid in water	99	88	2	0
25% solid in water	94	94	2	2
50% solid in water	91	85	68	66

Comparison of the activity remaining in compositions 3, 4, and 6 to the other compositions indicates that the borate salt significantly stabilizes enzyme activity in aqueous concentrates made from the present solid compositions.

Experiment 2

The components listed in Table 4 were mixed to form a solid cleaning composition. A portion of the solid cleaning composition was mixed with water and allowed to sit. The activity of enzyme in this aqueous mixture was then measured. The enzyme was measured by cleaning activity. Cleaning performance was measured in a ware washing machine. The performance scores were based on removal of baked-on oatmeal from chinaware. This cleaning is a known test for amylase activity.

Table 4 - Solid Compositions Including Stabilized Enzyme Used in Experiment 2

Composition (wt-%)

	9	10	11 (Control)
Sodium Carbonate	30	30	39
Sodium Silicate	6	6	6
Sodium Tripolyphosphate	25	25	28
Sodium Borate	10	7	
Nonionic Surfactant	3	3	3
Sodium EDTA	7	7	
DTPA (40% solution)	2.3	2.3	
Enzymes and minor ingredients*	10	10	21
Water of hydration	8	8	3

*Enzymes and minor ingredients include anti-etch (e.g., $ZnCl_2$ and $NaAlO_4$), filler (e.g., 8 wt-% sodium sulfate), enzyme, and the like.

Table 5 -- Amylase Cleaning Activity After Forming Aqueous Mixtures of Compositions 9 and 10

Formula	Amt Formula Used	Conditions	Aging Time (hr)	Aging Temperature	Cleaning Score*	Cleaning Result
9	10g pre + 10g wash	powder	0	-	1	very good
	10g	slurry	24	r.t.	3	very good
	20g	slurry	72	r.t.	6	good
	20g	slurry	120	r.t.	12	poor
	10g pre + 10g wash	slurry	24	120 °F	6	good
	10g	slurry	24	160 °F	6	good
	10g pre + 10g wash	slurry	24	160 °F	4	very good
10	10g pre + 10g wash	slurry	120	100 °F	1	very good
	10g pre + 10g wash	slurry	120	r.t.	5	good
	10g pre + 10g wash	slurry	24	r.t.	4	good
	10g pre + 10g wash	slurry	24	100 °F	2	very good
11	10 g	powder	0	-	3	very good
	10 g	slurry	24	r.t.	10	poor

* The cleaning score is a total from three cleaning tests, each of which was graded according to Table 6. Starch was cleaned from two different mugs and a bowl.

Table 6 - Amylase Starch Cleaning Scoring

Score	Description
0	No staining
1	None-Minimal staining
2	Minimal staining
3	Minimal-Moderate staining
4	Moderate staining
5	Moderate-Heavy staining
6	Heavy staining

Comparison of the control composition to the experimental compositions indicates that borate stabilized the amylase in these compositions.

Experiment 3

The components listed in Table 7 were mixed to form a solid cleaning composition. A portion of the solid cleaning composition was mixed with an equal weight of water and aged for 48 hours at 100 °F. The activity of enzyme in this aqueous mixture was then measured. The enzyme was assayed with commercially available reagents and methods. Briefly: Protease activity was determined using a standard test method developed by Genencor International, Inc. This method reports protease activity as GSU (Genencor Subtilisin Units). Amylase activity was measured by determining the amount of residual starch after exposure to amylase enzyme. A spectrophotometer was used to measure absorbance of iodine-starch solutions at 620 nm. High absorbance indicated high levels of remaining starch, and therefore low activity of amylase enzyme.

Table 7 - Solid Compositions Including Stabilized Enzyme Used in Experiment 3

Composition (wt-%)

Ingredient	12	13	14	15	16	17	18	19	20	21
Sodium Carbonate	30	30	2.0		30	30	30	2		28
Sodium Sulfate	25	35	53	65	40	30	40	58	70	32
Sodium Borate	10		10			10		10		10
Nonionic Surfactant	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7
Sodium Tripolyphosphate	24	24	24	24	24	24	24	24	24	24
Sodium Perborate Monohydrate	5.0	5.0	5.0	5.0						
Protease	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Amylase	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4

In these compositions, the solidification agent included sodium carbonate and water. The borate was supplied as boric acid except in composition 21 which employed borax. The nonionic surfactant included a low foaming linear alcohol alkoxylate sold under the tradename Plurafac SLF 18, an ethoxy-propoxy copolymer (sold under the tradename D-500), stearic monoethanolamide, and a polyether siloxane (sold under the tradename Abil B8852). The amylase was a commercially available product, alpha amylase, sold under the tradenames Purastar (e.g., Purastar ST 15000L and Purastar OxAm 4000E) by Genencor International. The protease was a commercially available product, subtilisin protease or high alkaline protease, sold under the tradenames Purafect (e.g., Purafect ST 4000L) and Properase (e.g., Properase 1000E) by Genencor International.

Table 8 -- Enzyme Activity After Forming Aqueous Mixtures of Compositions 12-21 (% Control)

	Composition									
Enzyme	12	13	14	15	16	17	18	19	20	21
Amylase	17	8	21	15	0.6	30	6	37	89	26
Protease	62	76	48	55	86					

In most of these compositions relatively little enzyme activity was observed even without aging of the composition. Comparison of the activity remaining in compositions 12, 17, and 21 to the activity in compositions 13 and 18 indicate that the borate salt significantly stabilizes enzyme activity in the high alkaline compositions. Little or no stabilization was observed otherwise. These compositions lack alkanol amine, silicone surfactant, and include only a low level of nonionic surfactant.

Experiment 4

The components listed in Table 9 were mixed to form a solid cleaning composition. A portion of the solid cleaning composition was mixed with an equal weight of water and aged for 64 hours at 100 °F. The activity of enzyme in this aqueous mixture was then measured. The enzyme was assayed with commercially available reagents and a standard test method developed by Genencor International, Inc. This method reports protease activity as GSU (Genencor Subtilisin Units).

Table 9 - Solid Compositions Including Stabilized Enzyme Used in Experiment 4

Ingredient	22 (wt-%)
Sodium Carbonate	31
Sodium Sulfate	8
Sodium Borate	10
Nonionic Surfactant	4.7
Sodium Tripolyphosphate	24
Sodium Silicate	6.1
Sequestrant	10
Salt	2
Protease	0.8
Water	3.6

In these compositions, the solidification agent included sodium carbonate and water. The nonionic surfactant included EO-PO block copolymer surfactant, alkanol ethoxylate surfactant, polyether siloxane, and stearic monoethanolamide. The sequestrant included EDTA, DTPA, sodium polyacrylate, and phosphino carboxylic acid. The salt included zinc chloride and sodium aluminate. The protease was a commercially available product, subtilisin protease or high alkaline protease, sold under the tradenames Purafect (e.g., Purafect OX 4000E) and Properase (e.g., Properase 1000E) by Genencor International.

Table 10 -- Enzyme Activity After Forming Aqueous Mixtures of Composition 22 (% Control)

	Purafect	Properase
Aqueous Mixture	93	84
Control (Powder)	71	90

Example 2 -- Solid Stabilized Enzyme Compositions Increase Slip Resistance of Floors

Liquid compositions of the solid compositions according to the present invention and including borate salt and lipase were shown to be effective for significantly increasing slip resistance of a tile floor.

Materials and Methods

A use dilution including composition Ex2 (Table 1, 0.16 % of solid) was applied each day to a tile floor, specifically a quarry tile floor, without rinsing. Dry and wet slip resistance measurements were taken over a 6-week period in kitchens of 2 restaurants. The 6 weeks included 2 weeks for baseline measurements and 4 weeks or measurements after application of composition Ex2. Before cleaning with the present composition (e.g., during the baseline period and before), the floor was cleaned daily with a conventional, commercially available floor cleaning composition.

Slip resistance was measured as coefficient of friction (COF) using an English XL Variable Incidence Tribometer according to ASTM F1679-02. The protocol was as follows. Fifteen quarry tiles were selected in each restaurant kitchen. In the main walking pathways and areas of concern (e.g., near fryers) every 5th tile was selected. The same 15 tiles in each restaurant were evaluated for COF each week. The COF of each tile was measured 4 times, once in each of 4 directions separated by 90°. Each tile was measured both wet and dry. The 60 measurements under each condition were averaged for each restaurant.

Results

Figure 1A illustrates the weekly results obtained for the COF (slip resistance) for the 15 tiles Restaurant 1. The COF of dry tile improved from an average baseline value of 0.73 to 0.82 through the 4-week test period. The COF of wet tile improved from an average baseline value of

0.33 to 0.46 through the 4-week test period. Each of these increases is significant with a confidence level exceeding 95%.

Figure 1B illustrates the weekly results obtained for the COF (slip resistance) for the 15 tiles Restaurant 2. The COF of dry tile improved from an average baseline value of 0.59 to 0.70 through the 4-week test period. The COF of wet tile improved from an average baseline value of 0.17 to 0.31 through the 4-week test period. Each of these increases is significant with a confidence level exceeding 95%.

Conclusion

Compositions according to the present invention significantly increase coefficients of friction for slippery surfaces, such as floors in restaurant kitchens.

Example 3 -- Solid Stabilized Enzyme Compositions Clean Grout

Compositions according to the present invention and including borate salt and lipase were shown to be effective for cleaning grout between tiles.

Materials and Methods

A use dilution of composition Ex2 (Table 1, 0.16 % of solid) was applied to a tile floor, specifically a quarry tile floor, without rinsing, as described in Example 2. The tile was photographed before and after application of the present composition.

Results

The photographs of Figures 2A and 2B illustrate that the present composition (Ex2) cleaned grout on a quarry tile floor in a restaurant kitchen. Figure 2A illustrates the floor before application of the present composition. Figure 2B illustrates the floor after application of the present composition.

Conclusions

The present compositions clean tile grout more effectively than conventional compositions.

It should be noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a mixture of two or more compounds. It should also be noted that the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this invention pertains.

The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

The claims defining the invention are as follows:

1. A solid cleaning composition comprising:

spore, bacteria, or fungi;

about 5 to about 35 wt-% monoethanolammonium borate, diethanolammonium borate, triethanolammonium borate, or a combination thereof;

solidification agent, wherein the solidification agent comprises polyethylene glycol, acid salt or mixture thereof; and

surfactant,

wherein the solid retains at least 70% initial activity of the spore, bacteria, or fungi, for at least one year.

2. The composition of claim 1, wherein the spore or bacteria comprises bacterial spore.

3. The composition of claim 1 or claim 2, comprising about 0.003 to about 35 wt-% nonionic surfactant.

4. The composition of claim 3, wherein the nonionic surfactant comprises:

nonionic block copolymer comprising of at least $(EO)_y(PO)_z$,

wherein y and z are independently between 2 and 100;

C_{6-24} alkyl phenol alkoxylate having 2 to 15 moles of ethylene oxide;

C_{6-24} alcohol alkoxylate having 2 to 15 moles of ethylene oxide;

alkoxylated amine having 2-20 moles of ethylene oxide;

or mixtures thereof.

5. The composition of claim 1 or claim 2, comprising about 0.05 to about 70 wt-% anionic surfactant.

6. The composition of claim 5, wherein the anionic surfactant comprises an alkyl benzene sulfonate.

7. The composition of claim 5 or claim 6, wherein the anionic surfactant comprises:

linear alkyl benzene sulfonate;
alpha olefin sulfonate;
alkyl sulfate;
secondary alkane sulfonate;
sulfosuccinate; or
mixtures thereof.

8. The composition of any one of claims 1 to 7, further comprising:

an effective amount of one or more antimicrobials;
an effective amount of one or more chelating agents;
or mixtures thereof.

9. The composition of any one of claims 1 to 8, wherein the solidification agent comprises carbonate.

10. The composition of claim 9, further comprising alkanol amine.

11. A solid cleaning composition according to claim 1, substantially as hereinbefore described with reference to any one of the examples.

Dated 30 July 2010
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