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(54) Title: ENZYME CLEANER FOR TEXTILES WITH STYRENE MALEIC ANHYDRIDE COPOLYMERS

(57) Abstract: An aqueous enzyme cleaning and protecting composition includes water, an enzyme, a surfactant, and styrene maleic anhydride. The enzyme includes at least one of a protease and an amylase. The surfactant includes at least one an anionic surfactant, a nonionic surfactant, and an amphoteric surfactant. The composition demonstrates enzyme activity.



ENZYME CLEANER FOR TEXTILES WITH STYRENE MALEIC ANHYDRIDE COPOLYMERS

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Background

Cleaning reagents containing enzymes have gained popularity in the consumer market. Laundry detergents and carpet/floor cleaners containing multiple enzymes are two successful examples of adapting enzyme technology. Enzymatic cleaners for pet care applications are particularly popular.

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Besides the cleaning performance to remove the mess/stain, anti-resoiling is another important performance measure. Resoiling is a phenomenon that occurs when previously cleaned spots attract dirt because residual dried, but sticky, surfactant remains on the carpet. Current enzyme cleaners have poor anti-resoiling performance (i.e., resoiling occurs).

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Compounds added to cleaners, e.g., such as compounds known for their superior anti-resoiling properties, can reduce the cleaning capability of enzyme cleaners. It is believed that this is due, at least in part, to a reduction in enzyme activity

Summary

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Thus, there is a need for an enzyme cleaner concept that can achieve high performance on (1) textile cleaning, (2) retained enzyme activities, and/or (3) anti-resoiling.

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The present disclosure provides enzyme cleaning and protecting compositions that are particularly useful for cleaning textiles, such as carpets and upholstery. The compositions include one or more enzymes, one or more surfactants, and a styrene maleic anhydride polymer component. Significantly, compositions of the present disclosure possess a good balance of cleaning ability, enzyme activity, and/or anti-resoiling ability (i.e., protecting ability).

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In one embodiment, the present disclosure provides an aqueous enzyme cleaning and protecting composition that includes: water; at least one enzyme selected from a protease and an amylase; at least one surfactant selected from an anionic surfactant, a nonionic surfactant, and an amphoteric surfactant; and a styrene maleic anhydride polymer component; wherein the composition demonstrates enzyme activity.

In certain embodiments, the present disclosure provides a method of cleaning and protecting a soiled textile. The method includes applying a composition of the present disclosure, and optionally, after a period of time, removing the composition from the textile.

The above summary of the present disclosure is not intended to describe each disclosed embodiment or every implementation of the present disclosure. The description that follows more particularly exemplifies illustrative embodiments. In several places throughout the application, guidance is provided through lists of examples, which examples may be used in various combinations. In each instance, the recited list serves only as a representative group and should not be interpreted as an exclusive list.

Detailed Description

The present disclosure provides aqueous enzyme cleaning and protecting compositions that are particularly useful for cleaning textiles, such as carpets and upholstery. The compositions include one or more enzymes, one or more surfactants, and a styrene maleic anhydride polymer component.

In one embodiment, the present disclosure provides an aqueous enzyme cleaning and protecting composition that includes: water; at least one enzyme selected from a protease and an amylase; at least one surfactant selected from an anionic surfactant, a nonionic surfactant, and an amphoteric surfactant; and a styrene maleic anhydride polymer component; wherein the composition demonstrates enzyme activity.

Significantly, compositions of the present disclosure possess a good balance of enzyme activity, cleaning ability, and anti-resoiling ability (i.e., protecting ability).

Compositions of the present disclosure “demonstrate enzyme activity” (e.g., protease and/or amylase). In certain embodiments, the compositions demonstrate protease and amylase activity. By this it is meant that the activity of an enzyme present in a composition of the present disclosure is not completely destroyed by the other components present in the composition (although there may be some decomposition of enzyme activity by one or more of the other components in the compositions). This would be a qualitative assay, indicating the presence of one or more active enzymes.

Enzyme activity for compositions of the present disclosure may be measured by a variety of known assays. For example, the protease activity of a cleaning formulation suspected of having protease activity can be determined in a variety of protease assays. A

specific example of a suitable enzyme assay is provided in the Examples section (the Enzyme Activity Test is provided specific for each type of enzyme). This specific example should not be considered a limiting example of a suitable assay.

Compositions of the present disclosure are typically evaluated for protease activity, and/or amylase activity, relative to a corresponding enzyme solution as a “control.” In evaluating the enzyme activity of a known test formulation, the “corresponding enzyme solution” is a “control” that contains the same enzyme(s) and same level of enzyme concentration (diluted with distilled water) as in the corresponding known test formulation. The enzyme activity is reported as a relative enzyme activity as a percentage of the enzyme activity of a corresponding enzyme solution (i.e., the “control” for a composition of the present disclosure with a known amount of enzyme).

In evaluating the enzyme activity of an unknown formulation (i.e., one with an enzyme but in an unknown amount), a “reference enzyme solution” can serve as a “reference sample” that contains a set of reference enzymes at a selected level of enzyme concentration (diluted with distilled water). This is referred to herein as the “control” for an unknown sample. The enzyme activity for the unknown formulation is reported as a relative enzyme activity as a percentage of the enzyme activity of the reference enzyme solution (i.e., the reference sample or “control” for an unknown formulation).

In certain embodiments, a composition of the present disclosure demonstrates an enzyme activity of at least about 10% of a control, or at least about 15% of a control, or at least about 20% of a control, or at least about 30% of a control (i.e., a “corresponding enzyme solution” for a test formulation containing a known amount of a protease or a “reference enzyme solution” for an unknown formulation with a protease in an unknown amount).

Cleaning ability may be measured by the Textile Cleaning Test (described in the Examples Section) and reported as a Delta E value, where Delta E represents the difference between the color of the virgin textile and the color of the stained and cleaned textile. A small Delta E is therefore desired. Compositions of the present disclosure preferably possess a cleaning ability represented by a Delta E value of no greater than about 10, no greater than about 8, no greater than about 6, and particularly between about 3 and about 6.5. It should be understood that Delta E values for cleaning may vary depending on the

textile color, fabric type, whether the textile has been initially treated with a fluorochemical treatment, type of stain, cleaning method, amount of cleaner, etc.

Anti-resoiling (i.e., protecting ability) may be measured by Resoiling Test (described in the Examples Section) and reported as a Delta E value, where Delta E represents the difference between the color of the virgin textile and the color of the cleaned and resoiled textile. A small delta E is therefore desired. Compositions of the present disclosure preferably possess an anti-resoiling ability (after 12 days of testing) represented by a Delta E value of no greater than about 10, no greater than about 8, no greater than about 6, and particularly between about 2 and about 4. It should be understood that the Delta E values for resoiling may vary depending on the textile color, textile type, whether the textile has been initially treated with a fluorochemical treatment, amount of cleaner, the amount of foot traffic (roughly correlated with the day count), weather (wet/snowy weather gives much more rapid soiling), etc.

Thus, as used herein, a composition that demonstrates “cleaning ability and protecting ability” preferably refers to a composition that possesses a cleaning ability (as measured by the Textile Cleaning Test) represented by a Delta E value of no greater than about 10 and a protecting ability (i.e., an anti-resoiling ability as measured by the Resoiling Test after 12 days of testing) represented by a Delta E value of no greater than about 10.

Enzymes

Compositions of the present disclosure include at least one enzyme. Such enzymes include at least one protease or amylase. The purpose of the enzyme is to break down adherent materials typically found in bodily fluids, such as blood, urine, vomit, feces, into forms that are readily dispersed into a water-based wash solution. Certain embodiments include a mixture of two or more enzymes, which may be of the same class of enzyme or of different classes of enzymes.

A wide variety of enzymes or mixture of enzymes, from a wide variety of sources, may be employed in the compositions of the present disclosure, provided that the selected enzyme is compatible with the other components of the composition. By “compatible” it is meant that the one or more enzymes are not completely inactivated by one or more of the other components of the composition.

While enzymes may be obtained commercially in a solid or liquid form, the liquid

form is preferred for greater convenience in dispersing the enzyme(s) during preparation of the compositions of the disclosure and for complete water dissolution of the enzyme(s).

Preferred enzymes are stable in an aqueous solution having a pH of about 7 to about 9.5, and retain sufficient activity per gram of enzyme protein when combined with the other components of the composition to economically solubilize and remove proteinaceous, carbohydrate-based, and/or lipid-based materials from textiles.

In certain embodiments, at least two different enzymes are included in compositions of the present disclosure. In certain embodiments, at least one enzyme from each of two different classes of enzymes (e.g., one protease and one amylase) is included in compositions of the present disclosure.

Suitable protease enzymes are, for example, the enzymes obtained from *Bacillus subtilis*, *Bacillus licheniformis*, and *Streptomyces griseus*. Suitable protease enzymes are one or more of the commercially available serine endoproteases. These enzymes preferably cleave protein links on the carboxyl side of hydrophobic amino acid residues, but are capable of cleaving most peptide links. They convert their substrates into small fragments that are readily dissolved or dispersed into a wash solution.

Exemplary proteases are commercially available under the trade names EVERLASE (e.g., EVERLASE 16L), LIQUANASE, SAVINASE (e.g., SAVINASE 16L), or ESPERASE (all available from Novozymes, Franklinton, NC), as well as PURAFECT (e.g., PURAFECT Prime L, PURAFECT L, or PURAFECT Ox) (available from Genencor, Rochester, NY). An exemplary protease is that from *Bacillus* sp. available from Sigma-Aldrich (St. Louis, MO), which is equivalent to SAVINASE 16L (Novozymes, Franklinton, NC).

Suitable amylase enzymes are, for example, the enzymes obtained from barley malt and certain animal glandular tissues. Preferred types of amylases include those which are referred to as alpha-amylases, beta-amylases, iso-amylases, pullulanases, maltogenic amylases, amyloglucosidases, and glucoamylases, as well as other amylase enzymes, including endo- and exo-active amylases. Such amylases are commercially available under the tradenames PURASTAR (e.g., PURASTAR ST or PURASTAR HP AmL) (available from Genencor), as well as STAINZYME, DURAMYL, or TERMAMYL (e.g., TERMAMYL 120 or TERMAMYL Ultra) (all available from Novozymes). An exemplary

amylase is Alpha-Amylase from *Bacillus Licheniformis* Type XII-A available from Sigma-Aldrich (St. Louis, MO), which is equivalent to TERMAMYL 120 (Novozymes).

In certain embodiments, compositions of the present disclosure include at least about 0.05 wt-%, of each of at least one enzyme product solution, in liquid form as supplied, based on the total weight of the composition. In certain embodiments, compositions of the present disclosure include up to about 10 wt-%, of each of at least one enzyme product solution, in liquid form as supplied, based on the total weight of the composition.

Surfactants

Any of a wide variety of surfactants (e.g., anionic, nonionic, amphoteric) may be used in the compositions of the present disclosure, so long as the surfactant is compatible with the other components of the composition, does not inactivate the enzyme(s) completely, and provides detergency desired to clean a soiled substrate. Mixtures of surfactants may be used in the compositions of the present disclosure. Such mixtures may include different surfactants of the same class (e.g., two anionic surfactants), or mixtures of different classes (e.g., anionic and nonionic surfactants).

Anionic Surfactants. The anionic surfactants can contain one or two hydrophobic groups and one or two water-solubilizing anionic groups. The hydrophobic group(s) should be large enough to make the surfactant sufficiently surface active, i.e., the total number of carbon atoms in all hydrophobic groups can particularly be at least about 8. The hydrophobic group is often an alkyl group, aryl group, or combination thereof. Examples of suitable hydrophobic groups include straight and branched octyl, decyl, lauryl (i.e., dodecyl), myristyl (i.e., tetradecyl), cetyl (i.e., hexadecyl), stearyl (i.e., octadecyl), dodecylbenzyl, naphthyl, xylyl, and diphenyl. Heteroatom-containing moieties may be present in the hydrophobic group, including, e.g., ester, amide, and ether groups. For example, some hydrophobic groups include an alkyl group connected to an ether or to a polyether segment. When more than one hydrophobic group is present, the length of the chain may be relatively short (e.g., two n-butyl groups).

The water-solubilizing anionic group can preferably be sufficiently polar to effectively solubilize the surfactant in water to allow formation of micelles. Suitable water-solubilizing anionic groups include, e.g., sulfonate, sulfate, sulfosuccinate, and carboxylate. The positive counterion(s) for the anionic group may be one or more alkali

metal ions (e.g., Na⁺, K⁺, or Li⁺), alkaline earth metal ions (e.g., Mg⁺⁺ or Ca⁺⁺), or ammonium ion (e.g., NH₄⁺, tetraalkyl ammonium ion, or protonated amine such as protonated triethanolamine (e.g., triethanolamine stearate has a protonated triethanolamine)). Optionally, the water-solubilizing anionic group may also contain a polyoxyethylene group of 1-15 monomeric units located between the hydrophobic group and the charged ionic group to form an ether sulfate, ether sulfonate or ether carboxylate group.

Preferred anionic surfactants include alkyl benzene sulfonates, alkyl ether sulfates, sulfonates, sulfosuccinates, and alkyl sulfates. Examples of suitable anionic surfactants include sodium lauryl sulfate, sodium myristyl sulfate, sodium lauryl ether (2) sulfate (i.e., C₁₂H₂₅(OCH₂CH₂)₂OSO₃⁻ Na⁺), ammonium lauryl ether sulfate (i.e., ammonium laureth sulfate or C₁₂H₂₅(OCH₂CH₂)₃OSO₃⁻ NH₄⁺), sodium decyl sulfate, ammonium myristyl ether sulfate, sodium nonylphenol polyglycol ether (15) sulfate, sodium C6-C8 α-olefin sulfonate, sodium dodecylbenzene sulfonate, sodium xylene sulfonate, sodium naphthyl sulfonate, sodium dihexyl sulfosuccinate, disodium lauryl ether sulfosuccinate (i.e., disodium laureth sulfosuccinate), sodium laurate, sodium stearate, sodium ether (5) stearate, potassium ricinoleate (potassium 12-hydroxy-9-octadecanoate), sodium myristoyl sarcosine, and sodium N-methyl-N-oleyl taurate. A preferred surfactant is sodium xylene sulfonate. Such anionic surfactants are commercially available from many suppliers (e.g., Stepan Company), many of whom are listed in the McCutcheon's Emulsifiers & Detergents directory, North America or International Editions (1996).

Exemplary anionic surfactants include sodium xylene sulfonate (a sulfonate type) available under the trade designation "STEPANATE SXS", disodium laureth sulfosuccinate (a sulfosuccinate type) available under the trade designation "STEPANMILD SL3-BA", and sodium lauryl sulfate (an alkyl sulfate type) available under the trade designation "STEPANOL WA-EXTRA", all from Stepan Company, Northfield, IL.

Nonionic Surfactants. Examples of nonionic synthetic detergents or surfactants are condensation products of ethylene oxide, propylene oxide, and/or butyleneoxide with (C8-C18)alkylphenols, (C8-C18)primary or secondary aliphatic alcohols, or (C8-C18)fatty acid amides. Other examples of nonionics include, e.g., tertiary amine oxides with one (C8-C18)alkyl chain and two (C1-C3)alkyl chains. The average number of moles of

ethylene oxide and/or propylene oxide present in the above various nonionics varies from 1-30; mixtures of nonionics, including mixtures of nonionics with a lower and a higher degree of alkoxylation, may also be used. Other examples of nonionic surfactants are those derived from sugars and fatty alcohols, for example, alkyl polyglucosides.

5 An example of a suitable nonionic surfactant is C8-C16 polyglucoside (e.g., such as the C8-C16 polyglucoside available from BASF (Florham Park, New Jersey) under the trade designation "GLUCOPON 425N"),

10 **Amphoteric Surfactants.** Suitable amphoteric (i.e., zwitterionic) surfactants (i.e., detergents) include alkylamido betaines, N-alkylamino acids, sulphobetaines, and condensation products of fatty acids with protein hydrolysates. An example of a suitable amphoteric surfactant is cocamidopropyl betaine (an alkyamidopropyl betaine) such as that available from Stepan Company, Northfield, IL, under the trade designation "AMPHOSOL CA".

Mixtures of the various types of surfactants may be used if desired.

15 In certain embodiments, the surfactant (in terms of surfactant solids) can generally be present in a composition of the present disclosure in an amount of between about 0.1 wt-% and about 5 wt-%, particularly between about 0.5 wt-% and about 4 wt-%, and more particularly between about 0.75 wt-% and about 3 wt-%, based on the total weight of the composition.

20 The lower the amount of surfactant, the less resoiling problems and the less the amount of styrene maleic anhydride polymer component needed to "offset" the surfactant (i.e., to counteract the tendency for residual surfactant left on the carpet to attract soil because it remains tacky). In one embodiment of the compositions of the present disclosure, a styrene maleic anhydride polymer component to surfactant solids ratio within a range of
25 about 0.5:1 to about 4:1 (solids only). For certain surfactants (e.g., ethoxylated alcohols), a higher ratio may be necessary to obtain a useful (i.e., non-resoiling) cleaner. For certain surfactants, a lower ratio may be necessary to obtain a more cost-effective cleaner.

Styrene Maleic Anhydride Polymer Component

30 The styrene maleic anhydride polymer component (i.e., styrene maleic anhydride - containing polymer component) is believed to be primarily responsible for the ability of the

compositions of the present disclosure to protect the substrate (e.g., carpet or upholstery) from restaining or resoiling.

In certain embodiments, the styrene maleic anhydride polymer component can include a reaction product of maleic anhydride, for example the reaction product of water to make a hydrolyzed styrene maleic anhydride solution, or the reaction product of an amine to make a styrene maleic anhydride amic acid.

Examples of useful styrene maleic anhydride containing polymer components include the hydrolyzed solutions Xiran SL40005-S40, Xiran SL25010-S25, Xiran SL40005-N30, Xiran SL40005-N30 amic acid, and Xiran SL25010-N15, all from Polyscope, Geleen, The Netherlands, and SMA-1000H, from Cray Valley, Exton Pennsylvania US.

The styrene maleic anhydride polymer component may be present in the composition in an amount which, upon cleaning a substrate with the composition, provides at least partial stain-blocking properties. If too little of the styrene maleic anhydride polymer is present, stain-blocking properties may be diminished; if too much polymer is present, the substrate can have a stiff and unpleasant feel and/or the cleaning ability of the composition is worse than if no styrene maleic anhydride polymer is used.

The styrene maleic anhydride polymer solids typically makes up at least about 0.1 weight percent (wt-%) and particularly at least about 0.5 wt-%, of polymer solids, based on the total weight of the composition. The styrene maleic anhydride polymer component typically is present in the compositions of the present disclosure in an amount of up to about 5 wt-% and particularly up to about 4 wt-%, of polymer solids, based on the total weight of the composition.

In one embodiment, the styrene maleic anhydride polymer is present in a ratio of about 1:1 to about 3:1 styrene to maleic anhydride.

Water and Optional Organic Solvents

In certain embodiments, water is present in compositions of the present disclosure in an amount of at least about 50 wt-% water, at least about 60 wt-%, at least about 70 wt-%, or at least about 80 wt-%, based on the total weight of the composition. In certain embodiments, water is present in compositions of the present disclosure in an amount of up to about 95 wt-% and particularly up to about 90 wt-%, based on the total weight of the composition.

Although it is possible that the compositions of the present disclosure contain no organic solvent, it may be necessary that a small amount of a compatible organic solvent be included in a composition. Such organic solvent may be used, e.g., because it has been included as part of the commercially available ingredients used (e.g., as a solvent or remnant of production), in order to dissolve one or more other ingredients within the composition, or to assist in dissolving oily stains. Examples of suitable organic solvents include those soluble in water, such as alcohols, ethers, glycol ethers, ketones, etc. A preferred organic solvent is a glycol ether (e.g., 1-methoxy-2-propanol). Generally, an organic solvent may be used in an amount of at least about 0.5 wt-% and particularly at least about 1 wt-%, based on the total weight of the composition. Generally, an organic solvent may be used in an amount of up to about 3 wt-% and particularly up to about 1 wt-%, based on the total weight of the composition.

Optional Additives

Various optional additives may be included in the compositions of the present disclosure.

For example, in compositions of the present disclosure, enzyme stabilizers may be used. Preferred enzyme stabilizers include boron compounds, calcium salts, or combinations thereof. More preferred, the enzyme stabilizer is a boron compound selected from the group consisting of boronic acid, boric acid, borate, polyborate, and combinations thereof. An exemplary boron compound is sodium borate available from Merck and Company, Rahway, NJ). If used, a boron compound is typically present in an amount of at least about 0.09 wt-%, and typically no more than about 10 wt-%, based on the total weight of the composition. If used, a calcium salt is typically present in an amount of at least about 0.01 wt-%, and typically no more than about 3 wt-%, based on the total weight of the composition.

Compositions of the present disclosure may optionally contain other ingredients, such as odor absorbers (e.g., chelate-free zinc salt dispersions, such as that available from Innovative Chemical Technologies, Cartersville, GA, under the trade designation "FLEXISORB OD-120-ZnR"), builders, fragrances, preservatives, embrittling agents (e.g., compounds that help keep residue brittle so it may be readily vacuumed when dry), sequestering agents, fluorochemicals, pH adjusters (e.g., acids such as HCl and bases such

as ammonium hydroxide), hydrotropes, and the like. If used, these added ingredients may be used in an amount of at least about 0.05 wt-% and particularly up to about 5 wt-%, based on the total weight of the composition.

5 Methods of Making and Using

Compositions of the present disclosure may be prepared by combining the ingredients, heated or unheated, with stirring until a uniform mixture is obtained.

10 In use, a composition of the present disclosure may be applied to a textile, particularly a carpet, using cleaning methods known in the industry (e.g., carpet cleaning industry). Generally, a method of cleaning and protecting a soiled textile involves: applying (e.g., by spraying) a composition as described herein to the soiled textile; and optionally, after a period of time (typically less than 10 minutes or less than 5 minutes), removing the composition from the textile.

15 If desired, the composition may not need to be removed from the composition. If it is removed, however, removing the composition from the textile will typically remove at least a portion of the soil (e.g., materials typically found in bodily fluids, such as blood, urine, vomit, feces, etc.), and provide protection as described herein. Removing can involve blotting dry, applying steam or liquid water to rinse the area, vacuuming the composition after it has dried, etc.

20 A preferred method involves spot cleaning and blotting. For example, in cleaning pet insults, any solid residue is removed, the composition applied to the soiled area, and optionally after a period of time (e.g., a few minutes) the soiled area is blotted dry.

25 An alternative method includes the step of hot water extraction, wherein the aqueous composition of the present disclosure is delivered to a textile, particularly a carpet, via a conventional delivery device, such as a high pressure pump. The spent composition is subsequently removed, e.g., by a wet vacuum system. Cleaning of the textile is performed during this flushing and rinsing process.

When a composition is used to clean a soiled textile, the cleaned textile is imparted with anti-resoiling properties provided by the composition of the present disclosure.

30 Significantly, using compositions of the present disclosure, subsequent steps of treating the cleaned textile with a fluorochemical repellent to provide soil resistance may be avoided.

EXAMPLES

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. These examples are merely for illustrative purposes only and are not meant to be limiting on the scope of the appended claims.

TEST METHODS

Enzyme Activity Test for Samples of the Present Disclosure

Activities of select protease and amylase enzymes in a given test cleaning formulation were measured according to the following assay descriptions. For each test cleaning formulation, enzyme activity in the test cleaning formulation was measured according to each of the enzyme assays described below, and the enzyme activity of a corresponding enzyme solution was also measured. "Corresponding enzyme solution" refers to a solution that contains the same enzyme(s) at the same concentration(s) as present in the test cleaning formulation, with no other components other than water present in the corresponding test cleaning formulation.

A relative enzyme activity for each of the enzyme assays described below was calculated using the general Equation I:

$$\text{Relative enzyme activity (percentage)} = 100 \times \frac{A_{\text{net}} \text{ of a test cleaning formulation}}{A_{\text{net}} \text{ of a corresponding enzyme solution}}$$

(Eqn. I)

where the term A_{net} was an absorbance value representing enzyme activity, as described in each of the enzyme assays below.

Protease Activity Assay: Protease activity was measured based on a colorimetric method using azocasein substrate. A 0.625% (w/v) azocasein (Sigma-Aldrich) solution in 0.5% (w/v) in sodium bicarbonate buffer, pH 8.3, was warmed up in 37°C water bath. Then, 0.8 milliliter (mL) of azocasein solution and a 0.2 mL aliquot of the unknown cleaning

formula were transferred to a 5 mL centrifuge tube, mixed by swirling and were incubated at 37°C in a water bath for 30 min. After that, 4 mL of 0.305 N trichloroacetic acid solution was added and mixed by swirling, then was filtered using 0.45 micrometer (µm) polypropylene membrane syringe filters into new 5 mL microfuge tubes. A 0.05 mL aliquot was transferred to a well plate and mixed with 0.15 mL of 500 millimolar (mM) NaOH. An absorbance reading at 440 nm (A_1) was then measured. The A_1 absorbance reading represented an absorbance of a sample that had an opportunity for protease enzyme to cleave the azocasein substrate.

In order to provide a suitable background sample that accounts for absorbance due to sample components other than cleavage products of azocasein (e.g., colorants in the test cleaning formulation), the following “background” sample was prepared as follows. A 0.625% (w/v) azocasein solution in 0.5% (w/v) in sodium bicarbonate buffer, pH 8.3, was warmed up in 37°C water bath. Then, 0.8 milliliter (mL) of the azocasein solution was transferred to a 5 mL centrifuge tube, mixed by swirling and was incubated at 37°C in a water bath for 30 min. After that, 4 mL of 0.305 N trichloroacetic acid solution was added and mixed by swirling, then a 0.2 mL aliquot of the test cleaning formulation was added and mixed briefly, and then was filtered using 0.45 micron (µm) polypropylene membrane syringe filters into new 5 mL microfuge tubes. A 0.05 mL aliquot was transferred to a well plate and mixed with 0.15 mL of 500 millimolar (mM) NaOH. An absorbance reading at 440 nm (A_0) was then measured. The A_0 absorbance reading represented a background absorbance of a sample that had not had an opportunity for protease enzyme to cleave the azocasein substrate.

A net absorbance value of the test cleaning formulation (i.e., “ A_{net} of test cleaning formulation”) was calculated, by subtracting A_0 from A_1 . The calculated A_{net} absorbance value represented a level of protease activity of the test cleaning formulation. Thus, for the Protease Activity Assay:

$$A_{\text{net}} = A_1 - A_0$$

In addition, a net absorbance value of a corresponding enzyme solution (i.e., “ A_{net} of corresponding enzyme solution”) was measured, after subjecting the corresponding enzyme solution to the same test protocol as above, in place of the test cleaning formulation.

As described above, a “corresponding enzyme solution” contained the same enzyme(s) at the same concentration(s) as present in the test cleaning formulation, with no other components other than water present in the corresponding test cleaning formulation.

5 **Amylase Activity Assay:** Amylase activity was measured based on a colorimetric method using starch azure substrate. A 1.0% (w/v) starch azure (Sigma-Aldrich) suspension in 1.125 mL of 20 mM sodium phosphate buffer with 50 mM sodium chloride, pH 7, and a 0.125 mL aliquot of test cleaning formulation were transferred to a microfuge tube, mixed by shaking and incubated for 30 minutes at room temperature on a rocker. Then, 0.5 mL
10 2.75 molar (M) acetic acid was added and mixed by swirling, followed by centrifugation for 5 minutes at 10,000 revolutions per minute (rpm). A 0.2 mL aliquot of the resulting supernatant was transferred to a well plate. An absorbance reading at 595 nm (A_1) was then measured. The A_1 absorbance reading represented an absorbance of a sample that had an opportunity for amylase enzyme to cleave the starch azure substrate.

15 In order to provide a suitable background sample that accounted for absorbance due to sample components other than cleavage products of starch azure (e.g., colorants in the test cleaning formulation), the following “background” sample was prepared as follows. A 1.0% (w/v) starch azure suspension in 1.125 mL of 20 mM sodium phosphate buffer with 50 mM sodium chloride, pH 7, was transferred to a microfuge tube, mixed by shaking and
20 incubated for 30 minutes at room temperature on a rocker. Then, 0.5 mL 2.75 molar (M) acetic acid was added and mixed by swirling, then 0.125 mL aliquot of test cleaning formulation was added, followed by centrifugation for 5 minutes at 10,000 revolutions per minute (rpm). A 0.2 mL aliquot of the resulting supernatant was transferred to a well plate. An absorbance reading at 595 nm (A_0) was then measured. The A_0 absorbance reading
25 represented a background absorbance of a sample that had not had an opportunity for amylase enzyme to cleave the starch azure substrate.

A net absorbance value of the test cleaning formulation (i.e., “ A_{net} of test cleaning formulation”) was calculated, by subtracting A_0 from A_1 . The calculated A_{net} absorbance value represented a level of amylase activity of the test cleaning formulation. Thus, for the
30 Amylase Activity Assay:

$$A_{\text{net}} = A_1 - A_0$$

In addition, a net absorbance value of a corresponding enzyme solution (i.e., “A_{net} of corresponding enzyme solution”) was measured, after subjecting the corresponding enzyme solution to the same test protocol as above, in place of the test cleaning formulation.

As described above, a “corresponding enzyme solution” contained the same enzyme(s) at the same concentration(s) as present in the test cleaning formulation, with no other components other than water present in the corresponding test cleaning formulation.

Enzyme Activity Test for an Unknown Cleaning Formulation

Activities of protease and amylase enzymes in a given unknown cleaning formulation can be measured according to the following enzyme assay descriptions, to obtain at least a qualitative indication of enzyme activity. Additionally, enzyme activity of a “reference enzyme solution” can be measured, for calculation of a relative enzyme activity of the unknown cleaning solution against the reference enzyme solution. “Reference enzyme solution” here refers to a solution that contains 0.5 weight percent of each of the enzyme product solutions of Protease 1 and Amylase 1, which are listed in Table 1, in distilled water. Alternatively, other enzyme product solutions at the equivalent enzyme activity level can be used.

A relative enzyme activity for each of the enzyme assays for an unknown cleaning formulation described below was calculated using the general Equation II:

$$\text{Relative enzyme activity (percentage)} = 100 \times \frac{A_{\text{net of an unknown cleaning formulation}}}{A_{\text{net of a reference enzyme solution}}}$$

(Eqn. II)

where the term A_{net} was an absorbance value representing enzyme activity, as described in each of the enzyme assays below.

Determination of Protease Activity for an Unknown Cleaning Formulation:

Protease activity of an unknown cleaning formula can be measured based on a colorimetric method using azocasein substrate. A 0.625% (w/v) azocasein (Sigma-Aldrich) solution in 0.5% (w/v) in sodium bicarbonate buffer, pH 8.3, is warmed up in 37°C water bath. Then, 0.8 milliliter (mL) of azocasein solution and a 0.2 mL aliquot of the unknown cleaning

formula are transferred to a 5 mL centrifuge tube, mixed by swirling and are incubated at 37°C in a water bath for 30 min. After that, 4 mL of 0.305 N trichloroacetic acid solution is added and mixed by swirling, then is filtered using 0.45 micrometer (µm) polypropylene membrane syringe filters into new 5 mL microfuge tubes. A 0.05 mL aliquot is transferred to a well plate and mixed with 0.15 mL of 500 millimolar (mM) NaOH. An absorbance reading at 440 nm (A_1) is then measured. The A_1 absorbance reading represents an absorbance of a sample that has had an opportunity for protease enzyme to cleave the azocasein substrate.

In order to provide a suitable background sample that accounts for absorbance due to sample components other than cleavage products of azocasein (e.g., colorants in the unknown cleaning formulation), the following “background” sample is prepared as follows. A 0.625% (w/v) azocasein (Sigma-Aldrich) solution in 0.5% (w/v) in sodium bicarbonate buffer, pH 8.3, is warmed up in 37°C water bath. Then, 0.8 milliliter (mL) of the azocasein solution is transferred to a 5 mL centrifuge tube, mixed by swirling and is incubated at 37°C in a water bath for 30 min. After that, 4 mL of 0.305 N trichloroacetic acid solution is added and mixed by swirling, then a 0.2 mL aliquot of the unknown cleaning formula is added and mixed briefly, and then is filtered using 0.45 micron (µm) polypropylene membrane syringe filters into new 5 mL microfuge tubes. A 0.05 mL aliquot is transferred to a well plate and mixed with 0.15 mL of 500 millimolar (mM) NaOH. An absorbance reading at 440 nm (A_0) is then measured. The A_0 absorbance reading represents a background absorbance of a sample that has not had an opportunity for protease enzyme to cleave the azocasein substrate.

A net absorbance value (A_{net}) is calculated, by subtracting A_0 from A_1 : The calculated A_{net} absorbance value represents a level of protease activity of the unknown cleaning formulation:

$$A_{\text{net}} = A_1 - A_0$$

In addition, a net absorbance value of a reference enzyme solution (i.e., “ A_{net} of a reference enzyme solution”) is measured, after subjecting the reference enzyme solution to the same test protocol as above, in place of the unknown cleaning formulation. As described above, a “reference enzyme solution” contains 0.5 weight percent of each of the enzyme

product solutions of Protease 1 and Amylase 1, which are listed in Table 1, or equivalent enzyme product solutions, in distilled water.

Determination of Amylase Activity for an Unknown Cleaning Formulation:

5 Amylase activity can be measured based on a colorimetric method using starch azure substrate. A 1.0% (w/v) starch azure suspension in 1.125 mL of 20 mM sodium phosphate buffer with 50 mM sodium chloride, pH 7, and a 0.125 mL aliquot of unknown cleaning formulation are transferred to a microfuge tube, mixed by shaking and incubated for 30 minutes at room temperature on a rocker. Then, 0.5 mL 2.75 molar (M) acetic acid is added
10 and mixed by swirling, followed by centrifugation for 5 minutes at 10,000 revolutions per minute (rpm). A 0.2 mL aliquot of the resulting supernatant is transferred to a well plate. An absorbance reading at 595 nm (A_1) is then measured. The A_1 absorbance reading represented an absorbance of a sample that had an opportunity for amylase enzyme to cleave the starch azure substrate.

15 In order to provide a suitable background sample that accounted for absorbance due to sample components other than cleavage products of starch azure (e.g., colorants in the test cleaning formulation), the following “background” sample was prepared as follows. A 1.0% (w/v) starch azure suspension in 1.125 mL of 20 mM sodium phosphate buffer with 50 mM sodium chloride, pH 7, was transferred to a microfuge tube, mixed by shaking and
20 incubated for 30 minutes at room temperature on a rocker. Then, 0.5 mL 2.75 molar (M) acetic acid was added and mixed by swirling, then 0.125 mL aliquot of unknown cleaning formulation was added, followed by centrifugation for 5 minutes at 10,000 revolutions per minute (rpm). A 0.2 mL aliquot of the resulting supernatant was transferred to a well plate. An absorbance reading at 595 nm (A_0) was then measured. The A_0 absorbance reading
25 represented a background absorbance of a sample that has not had an opportunity for amylase enzyme to cleave the starch azure substrate.

A net absorbance value of the test cleaning formulation (i.e., “ A_{net} of test cleaning formulation”) is calculated, by subtracting A_0 from A_1 . The calculated A_{net} absorbance value represents a level of amylase activity of the test cleaning formulation:

$$A_{\text{net}} = A_1 - A_0$$

In addition, a net absorbance value of a reference enzyme solution (i.e., “ A_{net} of a reference enzyme solution”) is measured, after subjecting the reference enzyme solution to the same test protocol as above, in place of the unknown cleaning formulation. As described above, a “reference enzyme solution” contains 0.5 weight percent of each of the enzyme product solutions of Protease 1 and Amylase 1, which are listed in Table 1, or equivalent enzyme product solutions, in distilled water.

Textile Cleaning Tests

A textile cleaning test, adapted from “Carpet and Rug Institute CRI Test Method 116” (dated July, 2010), was conducted for each test cleaning formulation using the following test procedure. One can (156 grams (g)) of “MIGHTY DOG” lamb flavored dog food (Purina, St. Louis, MO) and 20 mL of water was mixed by a “WARING” blender. Concentrated HCl was slowly added until the mixture reached a pH of 3.3. For carpet cleaning tests, a portion (2.5 +/- 0.1 g) of the food mixture was evenly distributed in a 5 cm diameter circular area by a tongue depressor across the beige nylon 6 residential carpet (Mohawk Industries, Calhoun, GA, “MOHAWK GENORA, STYLE PL-081”, color L015, factory fluorochemically-treated), then the food mixture was allowed to stain the carpet for 3 minutes. After removing the excess food mixture from the carpet, 7g of a test cleaning sample was sprayed on the stained area. 90 seconds after spraying, the stained area was scrubbed with a paper towel for 30 seconds with small circular strokes, and then the cleaning procedure was repeated an additional time. For fabric cleaning tests, the procedure was the same as for carpet, except that heavy white woven cotton fabric (#428, from Test Fabrics Inc., West Pittston PA), was used as the substrate and a water rinse step was added after the second scrubbing with cleaner. After drying the textiles at room temperature for 24 hours, the color difference (Delta E value) from virgin carpet was measured by a colorimeter (MINOLTA CR-200). The Delta E value was calculated according to Equation III (Eqn. III):

$$\text{Delta } E_{ab}^* = [(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2]^{1/2} \quad (\text{Eqn. III})$$

where L^* , a^* and b^* are coordinates in three dimensional color space for samples. Because Delta E represents the difference between the color of the virgin textile and the color of the stained and cleaned textile, a small Delta E is desirable.

5 Resoiling Test

 About 5 g (± 0.3 g) of each test cleaning formulation was applied, to tan nylon 6 factory fluorochemically-treated residential carpet (obtained from Mohawk Industries, Calhoun, GA under the trade designation "MOHAWK TWIN GROVE, STYLE 26346", color 732) in 2.2 inch (5.5 cm) diameter circles to represent spot cleaning. The carpet was
10 air-dried for several days, and then was subjected to foot traffic in a commercial setting for 12 days. The color difference (Delta E value) from virgin carpet was measured by a colorimeter (MINOLTA CR-200). The Delta E value was calculated according to Equation III (Eqn. III), presented above. As with the cleaning tests, Delta E represents the difference between the color of the virgin carpet and the color of the soiled carpet, so a small Delta E
15 is preferred; for example, Delta E values of no greater than 10, preferably no greater than 4, are desirable.

Stain Resistance Test

 Stain resistance was determined using the following test procedure. A 6 inch by 12
20 inch (15 cm by 30 cm) non-fluorochemically treated blue nylon 6,6 carpet sample (Beaulieu 02364 color "Blue Moon") was stained for 24 hours at room temperature by 20 mL of an aqueous staining solution contained inside a 2.5 inch (6.4 cm) diameter circular dam. The aqueous staining solution consisted of 0.007 wt% of Red Dye FD&C No. 40 in deionized water adjusted to a pH of 3.0 with 10% aqueous citric acid. Excess dye solution was then
25 rinsed from the carpet sample by placing the dyed carpet sample under a stream of deionized water until the water ran clear. The rinsed carpet sample was then extracted to dampness using a Bock Centrifugal Extractor and was then air-dried overnight at room temperature. The degree of staining of the carpet sample was then determined numerically by using a Minolta CHROMA METER CR-310 compact tristimulus color analyzer.

30 The color analyzer measured red stain color autochromatically on the red-green color coordinate as a "Delta a" (Δa) value as compared to the color of an unstained and untreated carpet sample. The Δa values were recorded to one place following the decimal

point and represented the average of 3 measurements. A greater Δa reading indicated a greater amount of staining from the red dye.

MATERIALS

- 5 Materials for the preparation of test samples included those materials listed in Table 1.

Table 1

Name	Description and source
1-Methoxy-2-propanol	1-Methoxy-2-propanol, obtained from Alfa Aesar, Ward Hill, MA
Control enzyme cleaner	An enzymatic cleaner, obtained from 3M Co., St. Paul, MN, under the trade designation “3M PRUVEN ENZYMATIC STAIN AND ODOR REMOVER”
AMPHOSOL CA	Cocamidopropyl betaine, an amphoteric surfactant (alkylamidopropyl betaine type), obtained from Stepan Company, Northfield, IL, under the trade designation “AMPHOSOL CA”, used at 35 wt% solids in water
Amylase 1	Alpha-Amylase from Bacillus Licheniformis Type XII-A, obtained from Sigma-Aldrich, St. Louis, MO, equivalent to TERMAMYL 120 (Novozymes), 1186 units/milligram (U/mg) protein
Deionized water	Deionized H ₂ O provided by 3M Co., St. Paul, MN
GLUCOPON 425N	A C8-C16 polyglucoside, a nonionic surfactant, obtained from BASF (Florham Park, NJ) under the trade designation “GLUCOPON 425N”, used at 50 wt% solids in water
Protease 1	Protease from Bacillus sp. obtained from Sigma-Aldrich, St. Louis, MO, equivalent to SAVINASE 16L (Novozymes, Franklinton, NC), 17 U/g

SMA 1000H	Styrene maleic anhydride copolymer ammonium salt solution, with 50% maleic anhydride, obtained from Cray Valley (Exton, PA), used at 30 wt% solids in water
Sodium benzoate	$\text{NaC}_7\text{H}_5\text{O}_2$, obtained from Alfa Aesar, Ward Hill, MA
Sodium borate	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ used as an enzyme stabilizer, obtained from Merck and Co., Inc., Rahway, NJ
STEPANATE SXS	Sodium xylene sulfonate, an anionic surfactant (sulfonate type), obtained from Stepan Company, Northfield, IL, under the trade designation "STEPANATE SXS", used at 43 wt% solids in water
STEPANMILD SL3-BA	Disodium laureth sulfosuccinate, an anionic surfactant (sulfosuccinate type), obtained from Stepan Company, Northfield, IL, under the trade designation "STEPANMILD SL3-BA", used at 30 wt% solids in water
STEPANOL WA-EXTRA	Sodium lauryl sulfate, an anionic surfactant (alkyl sulfate type), obtained from Stepan Company, Northfield, IL, under the trade designation "STEPANOL WA-EXTRA", used at 30 wt% solids in water
XIRAN SL40005-N30	Styrene maleic anhydride copolymer ammonium salt solution, with 40% maleic anhydride, obtained from Polyscope, Geleen, The Netherlands, used at 30 wt% solids in water
XIRAN SL40005-N30 amic acid	Styrene maleic anhydride amic acid copolymer solution, with 40% maleic anhydride, obtained from Polyscope, Geleen, The Netherlands, used at 30 wt% solids in water

XIRAN SL40005-S40	Styrene maleic anhydride sodium salt copolymer solution, with 40% maleic anhydride, obtained from Polyscope, Geleen, The Netherlands, used at 40 wt% solids in water
XIRAN SL25010-S25	Styrene maleic anhydride copolymer sodium salt solution, with 25% maleic anhydride, obtained from Polyscope, Geleen, The Netherlands, used at 25 wt% solids in water
XIRAN SL25010-N15	Styrene maleic anhydride copolymer ammonium salt solution, with 25% maleic anhydride, obtained from Polyscope, Geleen, The Netherlands, used at 15 wt% solids in water

EXAMPLES 1-15

Test cleaning formulations were prepared using the amounts summarized in Tables 2 and 3. Test cleaning formulations in Tables 2 and 3 included anionic, cationic, and amphoteric surfactants and several kinds of styrene maleic anhydride polymers. Numerical values in Tables 2 and 3 are weight percent values relative to the total weight of the composition including water. Polymer solutions, supplied with different percent solids, were generally added at weight percent values so that the concentration of polymer solids was constant for each formula at 1.8 weight percent (Ex1-Ex9). Ex10, Ex11, and Ex12 were included to demonstrate utility of the invention at lower percent polymer solids; Ex13, Ex14 and Ex15 demonstrate utility at higher percent polymer solids. Weight percent values of surfactant components are for the surfactant components listed in the Materials Table (Table 1), which were used as a mixture in water (as provided by the supplier). Weight percent values of protease and amylase enzymes refer to the enzyme solutions as provided by the supplier. The weight percents of DI water refer to added water (not including water provided with each component).

Table 2

Ingredient	Ex1	Ex2	Ex3	Ex4	Ex5	Ex6	Ex7	Ex8	Ex9
DI Water	89.33	89.73	89.73	89.73	89.00	89.33	89.33	89.33	89.33
STEPANATE SXS	3.0	3.0	3.0	3.0	3.0	--	2.5	--	--
STEPANOL WA-EXTRA	--	--	--	--	--	3.0	--	--	--
GLUCOPON 425N	--	--	--	--	--	--	--	3.0	--
STEPANMILD SL-3BA	--	--	--	--	--	--	0.5	--	--
AMPHOSOL CA	--	--	--	--	--	--	--	--	3.0
1-Methoxy-2-propanol	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
XIRAN SL40005-N30	6.0	6.0	--	--	--	6.0	6.0	6.0	6.0
XIRAN SL40005-N30 amic acid	--	--	6.0	--	--	--	--	--	--
SMA 1000H	--	--	--	6.0	6.0	--	--	--	--
Sodium benzoate	0.4	--	--	--	--	0.4	0.4	0.4	0.4
Sodium borate	0.09	0.09	0.09	0.09	--	0.09	0.09	0.09	0.09
Protease 1	0.09	0.09	0.09	0.09	0.5	0.09	0.09	0.09	0.09
Amylase 1	0.09	0.09	0.09	0.09	0.5	0.09	0.09	0.09	0.09
Totals	100	100	100	100	100	100	100	100	100
Polymer solids	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8

Table 3

Ingredient	Ex10	Ex11	Ex12	Ex13	Ex14	Ex15
DI Water	92.73	92.73	85.73	85.73	75.73	85.73
STEPANATE SXS	3.0	3.0	3.0	3.0	3.0	3.0
1-Methoxy-2-propanol	1.0	1.0	1.0	1.0	1.0	1.0

SMA 100H	--	3.0	--	--	--	--
XIRAN SL40005-S40	--	--	--	--	--	10.0
XIRAN SL25010-S25	3.0	--	--	10.0	--	--
XIRAN SL25010-N15	--	--	10.0	--	20.0	--
Sodium borate	0.09	0.09	0.09	0.09	0.09	0.09
Protease 1	0.09	0.09	0.09	0.09	0.09	0.09
Amylase 1	0.09	0.09	0.09	0.09	0.09	0.09
Totals	100	100	100	100	100	100
Polymer solids	0.75	0.90	1.5	2.5	3.0	4.0

The test cleaning formulations were evaluated individually for protease and amylase activity according to each respective Enzyme Activity Test, using separate samples to evaluate each of the enzyme activities for each of the test cleaning formulas. The calculated mean relative activity values were as summarized in Table 4 (“SD” refers to “Standard Deviation”, with n=3). The percentage values in Table 4 are the mean percentages of the relative enzyme activity calculated according to Eqn. 1 and reported as a percentage of the corresponding enzyme solution used as a control. Enzyme activities for each formula were considered acceptable.

Table 4

Example	Protease 1		Amylase 1	
	Mean	SD	Mean	SD
Ex1	43%	4%	95%	8%
Ex2	45%	2%	93%	5%
Ex3	29%	3%	109%	7%
Ex4	40%	5%	95%	8%
Ex5	55%	2%	62%	2%
Ex6	21%	3%	81%	6%
Ex7	46%	7%	76%	6%
Ex8	55%	5%	92%	5%
Ex9	66%	7%	34%	3%
Ex10	54%	1%	82%	6%

Ex11	47%	6%	80%	5%
Ex12	38%	1%	33%	4%
Ex13	29%	1%	45%	0.1%
Ex14	24%	1%	23%	4%
Ex15	36%	1%	144%	13%

Several exemplary test cleaning formulas, as well as the control enzyme cleaner, were evaluated individually according to the Textile Cleaning Tests. The measured Delta E values were as summarized in Table 5 (n=4) for the carpet cleaning test and in Table 6 (n=3) for the fabric cleaning test. Textile cleaning abilities of each of the test cleaning formulations were considered equivalent to the control and therefore acceptable.

Table 5

Example	Delta E	SD
Ex2	4.6	1.3
Ex3	3.0	0.5
Ex4	3.6	1.3
Control enzyme cleaner	3.2	0.8

Table 6

Example	Delta E	SD
Ex2	5.6	0.4
Ex3	4.8	0.8
Ex4	5.5	1.6
Control enzyme cleaner	6.5	0.4

Several test cleaning formulas, as well as the control enzyme cleaner, were evaluated individually according to the Resoiling Test. The measured Delta E values were as summarized in Table 7. The values are the average of 10 individual samples. Delta E

represents the difference between the color of the virgin carpet and the color of the soiled carpet, so a small Delta E was desired.

Table 7

Example	Delta E	SD
Ex2	2.2	0.3
Ex3	2.3	0.3
Ex4	2.4	0.2
Control enzyme cleaner	4.1	0.2

5

In another experiment, test cleaning formulations were evaluated individually according to the Stain Resistance Test. A 10 gram aliquot of each cleaning solution was sprayed onto the carpet in a 5.5 cm diameter area and allowed to dry, then red dye was applied over the same area per the Stain Resistance Test. A greater Delta a (Δa) reading indicated a greater amount of staining from the red dye, so smaller values were desired. The measured Δa values were as summarized in Table 8 (n=3).

10

Table 8

Example	Δa	SD
Ex1	25.4	0.7
Ex2	27.4	1.0
Ex3	7.6	1.5
Ex4	32.5	0.6
Ex13	32.5	2.8
Ex15	28.3	3.3

15

Example formulations using a styrene maleic anhydride copolymer having maleic anhydride:styrene ratios closer to 1:1 performed well; for example, a maleic anhydride:styrene ratio of 40:60 worked particularly well (Ex1-Ex 4). The residual stains from treatment with these formulations were light in color and had acceptably low Delta a

values. Other styrene maleic anhydride polymers having a maleic anhydride:styrene ratio of 25:75 also showed good stainblocking performance when used at higher polymer solids concentrations (Ex13 and Ex15).

Various modifications and alterations to this disclosure will become apparent to those skilled in the art without departing from the scope and spirit of this disclosure. It should be understood that this disclosure is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the disclosure intended to be limited only by the claims set forth herein as follows.

What is claimed is:

1. An aqueous enzyme cleaning and protecting composition comprising:
Water;
5 an enzyme, wherein the enzyme comprises at least one of a protease and an amylase;
a surfactant, wherein the surfactant comprises at least one an anionic surfactant, a nonionic surfactant, and an amphoteric surfactant; and
a styrene maleic anhydride polymer component;
10 wherein the composition demonstrates enzyme activity.
2. The composition of claim 1, which demonstrates enzyme activity of at least about 10% of a control.
- 15 3. The composition of claim 1, wherein the surfactant is present in an amount of at least about 0.1 wt% of surfactant solids, based on the total weight of the composition.
4. The composition of claim 4, wherein the surfactant is present in an amount of up to about 5 wt% of surfactant solids, based on the total weight of the composition.
20
5. The composition of claim 1, wherein the styrene maleic anhydride polymer component is present in an amount of at least about 0.1 wt% of polymer solids, based on the total weight of the composition.
- 25 6. The composition of claim 1, wherein the styrene maleic anhydride polymer component is present in an amount of up to 5 wt-% of polymer solids, based on the total weight of the composition
7. The composition of claim 1, wherein the styrene maleic anhydride polymer
30 component is present at a ratio of about 1:1 to about 3:1 styrene to maleic anhydride.

8. The composition of claim 1, wherein the styrene maleic anhydride polymer component is modified with an amine to form a styrene maleic anhydride amic acid polymer.
- 5 9. A method of cleaning and protecting a textile, the method comprising:
applying a composition of claim 1 to the textile; and
optionally, after a period of time, removing the composition from the textile.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/033238

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D1/14 C11D1/22 C11D1/66 C11D1/90 C11D3/37
C11D3/386

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/78906 A1 (RECKITT BENCKISER INC) 28 December 2000 (2000-12-28)	1-7,9
Y	pages 13,15; claim 4; examples 1-3,21; table 1 page 10, lines 5-13; examples 7-20; table 1 page 6, lines 21-27 page 3, lines 13-23	1,4-7
X	----- CN 102 392 374 B (UNIV SOOCHOW) 10 July 2013 (2013-07-10) pages 1-2; claim 1	1-7,9
X	----- WO 2012/028203 A1 (ECOLAB INC) 8 March 2012 (2012-03-08)	1-3,5
Y	pages 18-19	1,5
A	pages 22-24,26 pages 28-29	9
	----- -/-	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

27 July 2016

Date of mailing of the international search report

04/08/2016

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Kanbier, Titia

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/033238

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 695 999 A (FORGIONE P S ET AL) 3 October 1972 (1972-10-03)	1,2,5-9
Y	column 1, lines 54-60 column 4, lines 24-27,34-35 column 5, lines 27-31; examples 3-5,11-13 -----	1,5-7
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