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BIO-SOAKING PERFORMANCES

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ABSTRACT OF THE DISCLOSURE

Biological cleaning composition containing an enzyme and, as an oxidizing agent, an alkali-metal monopersulfate triple salt. Preferred enzymes are proteolytic subtilisin enzymes. A preferred monosulfate triple salt is

$$[2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4]$$

This is a continuation of application, Ser. No. 75,716 filed Sept. 25, 1970, now abandoned.

This invention relates to a biological enzyme composition containing an enzyme and an oxidizing agent.

Cleaning preparations including enzymes have been used with oxidizing agents. Sodium perborate has been generally used. Other oxidizing agents have been suggested, but they have not been favored because of lack of stability or poorer cleaning capability than sodium perborate.

It is an object of this invention to provide a biological cleaning composition containing a stable oxidizing agent which is a superior biological detergent in cleaning capability, particularly in the cleaning of proteinic blood stains.

Other objects will be apparent from consideration of the specification.

In accordance with cermtain of its aspects, this invention relates to a biological cleaning composition containing a proteolytic enzyme and an alkali-metal monopersulfate triple salt.

The proteolytic enzymes which are employed in the instant invention are active upon protein matter and catalyze digestion or degradation of such matter when present as in linen or fabric stain in a hydrolysis reaction. The enzymes are effective at a pH range of 4–12, such as usually prevails in detergent cleaning procedures. Moreover, they may be effective even at moderately high temperatures so long as the temperature does not degrade them. Some proteolytic enzymes are effective at up to 70° C. and higher. They are also effective at ambient temperature and lower to about 20° C. Particular examples of proteolytic enzymes which may be used in the instant invention include pepsin, trypsin, chymotrypsin, papain, bromelin, colleginase, keratinase, carboxylase, amino peptidase, elastase, subtilisin, and aspergillopepidase A and B. Preferred enzymes are subtilisin enzymes manufactured and cultivated from special strains of spore-forming bacteria, particularly *Bacillus subtilis*. Furthermore, it is preferred that the enzyme be substantially free from sulfhydryl groups or disulfide bonds which may inhibit some of the active oxygen of the oxidizing agent.

Metalloproteases which contain divalent ions, such as calcium, magnesium or zinc, bound to their protein chains are of particular interest.

It is within the scope of this invention to use other enzymes which have amylolytic or lipolytic activity together with the proteolytic enzyme or to use an enzyme which contains such other activity together with proteolytic activity.

The enzyme preparations are generally extremely fine, often substantially impalpable, powders. In a typical powdered enzyme preparation, the particle diameter is mainly below 0.15 mm., generally above 0.01 mm., e.g., about 0.1 mm. For example, as much as 75% of the material may be 0.149 mm. or smaller. On the other hand, the spray-dried granules are usually of very much larger particle size, with the major portion of the granules being at least about 0.2 mm. in diameter, e.g., about 0.3 or 0.4, or even 0.5, 1 or 2 mm.

The enzyme preparations are generally diluted with salts such as calcium sulfate and inert materials. Chemically, they are typically stable in the pH of about 6 to 11, and at an alkaline pH of about 8.5 to 10 they can withstand temperatures of about 50° C. to 70° C. with relatively little decomposition for time periods varying from 2 hours at the higher temperatures to more than 1 day at the lower temperatures. Different proteolytic enzymes have different degrees of effectiveness in aiding in the removal of stains from textiles and linen.

The alkali-metal (that is, lithium, sodium, potassium, and ammonium) monopersulfate triple salts used in practice of the instant invention are particularly desirable since other alkali-metal monopersulfate salts are not sufficiently stable to produce desirable cleaning with the enzyme and other alkali-metal persulfate salts, such as the dipersulfates, are far inferior to the monopersulfate triple salt in cleaning effectiveness.

The preferred active oxygen compound, potassium monopersulfate triple salt, available commercially under the trademark Oxone, can be prepared with potassium monopersulfate, potassium bisulfate, and potassium sulfate as a triple salt with a mole ratio of constituents of about 2:1:1, that is, $[2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4]$. About 50% by weight of the triple salt is the active oxygen compound, potassium monopersulfate. When the triple salt is added to water, a pH of about 2–3 is obtained. A convenient method for preparing the triple salt is to react a mixture of monopersulfuric acid and a sulfuric acid with an alkali metal carbonate or hydroxide and drying the triple salt reaction product.

The active oxygen content of the alkali metal monopersulfate triple salt is about 5% by weight. A preferred range of proportions of the monopersulfate triple salt is one which provides an active oxygen concentration of about 1–50 p.p.m., more preferably 3–25 p.p.m., for example, 5–15 p.p.m., of active oxygen to wash water. The proportions of salt can, therefore, be readily calculated if one knows how much of total formulation is to be added to wash water. Detergent formulations may be designed for use in proportion of about 0.2–0.5% for soaking in water or about 0.1–0.2 or 0.3–1% for washing in water.

The enzyme concentration can be varied widely. Typically, an enzyme having a proteolytic activity of about 1.5 Anson units per gram is present in amount which provides about 1 to 40 p.p.m., more preferably about 2–8 p.p.m. of the enzyme in the wash water. The optimum proportion of enzyme to be used in a detergent composition containing triple salt will, of course, depend upon the effective enzyme content of the enzyme preparation. As with triple salt content, the quantity of enzyme to be used for stains susceptible to enzyme action will be dependent upon a number of factors, particularly time, temperature, and proportions of triple salt.

The enzyme and triple salt may be used together, as in the water used for a pre-rinse of the soiled clothes, without any surface-active detergent being present. It is preferable, however, to mix these ingredients into a surface-active detergent composition, such as a heavy-duty built granular detergent composition or more preferably in a soaking detergent composition.

The surface active agent which may be employed may be any commonly used compound having surface active or detergent properties. Most preferred are those water-soluble surface active compounds having an anionic or nonionic properties. Anionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and an anionic solubilizing group. Typical examples of anionic solubilizing groups are sulfonate, sulfate, carboxylate, and phosphate. Examples of suitable anionic detergents which fall within the scope of the invention include the soaps, such as the water-soluble salts of higher fatty acids or rosin acids, such as may be derived from fats, oils and waxes of animal, vegetable or marine origin, e.g., the sodium soaps of tallow, grease, coconut oil, tall oil, and mixtures thereof, and the sulfated and sulfonated synthetic detergents, particularly those having about 8 to 26, and preferably 12 to 22, carbon atoms to the molecule.

As examples of suitable synthetic anionic detergents, there may be cited the higher alkyl mononuclear aromatic sulfonates, such as the higher alkyl benzene sulfonates, containing from 10 to 16 carbon atoms in the alkyl group in a straight or branched chain, e.g., the sodium salts of decyl, undecyl, dodecyl (lauryl), tridecyl, tetradecyl, pentadecyl, or hexadecyl benzene sulfonate; and the higher alkyl toluene, xylene, and phenol sulfonates; alkyl naphthalene sulfonate, ammonium diamyl naphthalene sulfonate, and sodium dinonyl naphthalene sulfonate; sulfated aliphatic alcohols such as sodium lauryl and hexadecyl sulfates, triethanolamine lauryl sulfate, and sodium oleyl sulfate; sulfated alcohol ethers, such as lauryl, tridecyl, or tetradecyl sulfates including 2–4 ethylene oxide moieties; sulfated and sulfonated fatty oils, acids or esters such as the sodium salts of sulfonated castor oil and sulfated red oil; sulfated hydroxyamides such as sulfated hydroxyethyl lauramide; sodium salt of lauryl sulfoacetate; sodium salt of dioctyl sulfosuccinate; and the sodium salt of oleyl methyl tauride.

Other anionic surface active agents which may be employed in the practice of this invention include olefin sulfonates, typically containing 8–25 carbon atoms.

Also included within the ambit of the invention are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g., coconut oil monoglyceride monosulfate, tallow diglyceride monosulfate; and the hydroxy sulfonated higher fatty acid esters such as the higher fatty acid esters of low molecular weight alkylol sulfonic acids, e.g., oleic acid ester of isethionic acid.

Nonionic surface active agents are those surface active or detergent compounds which contain an organic hydrophobic group and a hydrophilic group which is a reaction product of a solubilizing group such as carboxylate, hydroxyl, amido or amino with ethylene oxide or with the polyhydration product thereof, a polyethylene glycol.

As examples of nonionic surface active agents there may be noted the condensation products of alkyl phenols with ethylene oxide, e.g., the reaction product of isooctyl phenol with about 6 to 30 ethylene oxide units; condensate products of alkyl thiophenols with 10 to 15 ethylene oxide units; condensation products of higher fatty alcohols such as tridecyl alcohol with ethylene oxide; ethylene oxide addends of monoesters of hexahydric alcohols and inner ethers thereof such as sorbitan monolaurate, sorbitol monoleate and mannitan monopalmitate and the condensation products of propylene glycol with ethylene oxide.

Cationic surface active agents may also be employed. Such agents are those surface active detergent compounds

which contain an organic hydrophobic group and a cationic solubilizing group. Typical cationic solubilizing groups are amine and quaternary groups.

As examples of suitable synthetic cationic detergents there may be noted the diamines such as those of the type $RNHC_2H_4NH_2$ wherein R is an alkyl group of about 12 to 22 carbon atoms, such as N-aminoethyl stearyl amine and N-laminoethyl myristyl amine; amide-linked amines such as those of the type $R'CONHC_2H_4NH_2$ wherein R' is an alkyl group of about 12 to 18 carbon atoms, such as N-amino ethyl-stearyl amide and N-amino ethyl myristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group of about 12 to 18 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including such 1 to 3 carbon alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen, acetate and methosulfate. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl-stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, methyl-ethyl-dilauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulfates and acetates.

The surface active compounds which are used in the most preferred aspects of this invention are those having anionic or nonionic properties. The most highly preferred water soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono-, di- and triethanolamine), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of the higher alkyl benzene sulfonates, the higher alkyl sulfates, and the higher fatty acid monoglyceride sulfates. The particular salt will be suitably selected depending upon the particular formulation and the proportions therein.

The surface active agent is typically present in amount of about 5–95% by weight of the detergent composition, preferably 10–25% by weight.

The enzyme may be present in powdered form admixed into the detergent formulation.

In addition to the materials described above, the detergent composition of the invention may include a builder for the detergent. The builder may be any of the water-soluble inorganic builder salts commonly known in the art, or it may be a water-soluble organic sequestering agent such as sodium nitrilotriacetate, or mixtures thereof.

The water-soluble inorganic builder salts may be suitable alkali metal, alkaline earth metal, or heavy metal salt or combinations thereof. Ammonium or an ethanol-ammonium salt in a suitable amount may be added also, but generally the sodium and potassium salts are preferred. Examples are the water-soluble sodium and potassium phosphates, silicates, carbonates, bicarbonates, borates, sulfates and chlorides. Particularly preferred builder salts are the alkaline builder salts such as polyphosphates, silicates and borates.

In the water-soluble inorganic builder salt mixtures used in the detergent compositions, it is often preferred to have present a mixture of sodium tripolyphosphate and sodium or potassium bicarbonate, such as a combination or mixture of salts wherein the bicarbonate to tripolyphosphate ratio is selected from the range of about 1:1 to about 3:1.

Both Phase I and Phase II sodium tripolyphosphate and mixtures thereof may be successfully used in the compositions. The usual commercial tripolyphosphate consists mainly of the Phase II material. The commercial tripolyphosphate material is usually essentially tripolyphosphate, e.g., 87–95%, with small amounts, e.g., 4–13%, of other phosphates, e.g. pyrophosphate and orthophosphate. Sodium tripolyphosphate in its hydrated form may be used also. Trisodium orthophosphate may be used in the amounts indicated.

The sodium or potassium bicarbonate is an effective buffer. The bicarbonate may be incorporated directly as anhydrous bicarbonate or in the form of sesquicarbonate, a hydrate containing both bicarbonate and carbonate.

Other suitable builder salts which may be present include the water-soluble sodium and potassium silicates, carbonates, borates, chlorides and sulfates.

Generally, when present the builder salt is employed in amount in the range of about 20–90%, preferably at least 25% (e.g. 35 to 80%) of the detergent composition.

The composition may also contain polymeric additives such as sodium carboxymethylcellulose or polyvinyl alcohol (e.g. in amount of about 0.1–5%) or other polymeric additives to inhibit redeposition of soil. Minor amounts of optical brighteners may be present, as in proportions in the range of about 0.01 to 0.15%; examples of such brighteners are the stilbene brighteners such as sodium-2-sulfo-4-(2-naphto-1,2 triazole) stilbene; disodium 4,4'-bis(4-anilino-6-morpholino-s-triazin-2-yl-amino) stilbene disulfonate or disodium 4,4'-bis(4,6-dianilino-s-triazin-2-yl-amino) stilbenedisulfonate; and the oxazole brighteners, having for example a 1-phenyl-2-benzoxazole ethylene structure. Perfumes, coloring agents and preservatives may also be included.

The enzyme and triple salt may be added in powdered form to the detergent composition and mixed therewith, as by dry blending. To improve the stability of the compositions, one or more of these ingredients may be protected from the atmosphere or from contact with the others. It is within the broader scope of the invention to supply separate packets (e.g. in moisture proof wrappings) of these ingredients for addition to the wash water.

The compositions of this invention may be used for washing for short periods, e.g. 5 to 45 minutes, in cool water, e.g. at 20–40° C., or in warm or hot water, e.g. at 50°, 60° or 70° C., or even at or near the boil. They may also, if desired, be used for long period soaking at room temperature or in hot water, for example, for several hours or overnight.

The following examples are given to illustrate further this invention. In these examples, as in the rest of the application, all proportions are by weight unless otherwise indicated.

EXAMPLE 1

A detergent composition having the following formula is prepared.

Component:	Parts, percent
Sodium dodecyl benzene sulfonate	28
Pentasodium tripolyphosphate	30
Sodium silicate (SiO_2/Na_2O=2/1)	6
Sodium carboxymethyl cellulose	0.8
Tetraanilino stilbene brightener	0.2
Perfume	0.2
Sodium sulfate and moisture, balance.	

0.7% subtilisin enzyme (Alcalase) having a proteolytic activity of 1.5 Anson Units per gram and various amounts of active oxygen compounds are added to this detergent to provide active oxygen in amounts indicated in the table below. The active oxygen compounds employed are the monopersulfate triple salt Oxone

$$[2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4],$$

sodium perborate tetrahydrate and potassium dipersulfate.

Two standard EMPA swatches stained with non-fixed blood are washed by shaking overnight at room temperature in one liter of solution containing 5 g. of soaking detergent containing varying amounts of active oxygen compound. The differences of reflectance readings before and after soaking and the benefit from the addition of active oxygen compound (ΔRd) are indicated in the table below:

TABLE

Active oxygen compound	P.p.m. of active oxygen in bath	Δ Rd	Active oxygen compound
None	0	43.5	
Oxone	1	44	0.5
Do	2	48	4.5
Do	5	59	15.5
Do	10	56	12.5
None	0	44	
Sodium perborate tetrahydrate	5	46	2
None	0	41	
Potassium dipersulfate	1	41	0
Do	2	41.5	0.5
Do	5	42.5	1.5
Do	10	44.5	3.5
Do	20	47.5	6.5
Do	50	50	9.0

It is apparent from the data set forth in the table above that the composition of the invention containing proteolytic enzyme and monopersulfate triple salt is superior in removing blood stains to compositions containing the same enzyme and sodium perborate tetrahydrate or dipersulfate salt.

The subtilisin enzyme "Alcalase" used in the foregoing examples is characterized as having its maximum proteolytic activity at a pH of 8–9. This activity as measured on the commercial enzyme available from Novo Industri A/S, Copenhagen, Denmark, is about 1.5 Anson units per gram of enzyme. The commercial enzyme is a raw extract of *Bacillus subtilis* culture.

EXAMPLE 2

Compositions containing Alcalase and Oxone as in Example 1 which are added to detergent having the formulation indicated below also produce superior increases in cleaning capability when stained fabrics are washed with such detergents for one-half hour at 50° C. in a solution containing 0.5% of the detergent.

Component:	Parts, percent
Linear sodium tridecylbenzene sulfonate	6.7
Sodium silicate	5.1
Pentasodium tripolyphosphate	70.0
Dimorpholine stilbene brightener	0.3
Oxazole brightener	0.03
Perfume	0.15
Sodium sulfate and moisture, balance.	

It will be apparent to one skilled in the art that various modifications of the foregoing examples may be made thereto.

I claim:

1. The process of cleaning proteinic blood stains which comprises washing or soaking proteinic blood stained material in an aqueous bath containing a biological cleaning composition consisting essentially of a proteolytic enzyme effective at a pH range of 4–12 in amount corresponding to about 1–40 p.p.m. based on a proteolytic activity of about 1.5 Anson units per gram when said composition is dissolved in water and an alkali metal monopersulfate triple salt in amount to provide about 1–50 p.p.m. of active oxygen when said composition is dissolved in water.

2. The process as claimed in claim 1 wherein said composition also includes about 5–95% by weight of a synthetic surface-active agent and about 20–90% by weight of a water-soluble detergent builder salt.

3. The process as claimed in claim 1 wherein said proteolytic enzyme is a subtilisin enzyme.

4. The process as claimed in claim 1 wherein said triple salt is [$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$].

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