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[54] **PROCESS OF CLEANING CLOTH**

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[63] Continuation-in-part of Ser. No. 817,197, April 17, 1969, abandoned, and a continuation of Ser. No. 6,942, Jan. 29, 1970, abandoned.

[52] **U.S. Cl.** **8/111,** 252/DIG. 12, 252/89, 252/95, 252/99, 252/105, 252/186

[51] **Int. Cl.** **D06l 3/02**

[58] **Field of Search** 8/111; 252/DIG. 12, 252/95, 99, 89, 186, 105

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[57] **ABSTRACT**

Detergent composition for soaking or washing containing organic detergent, enzyme and hydroxylamine compound or hydrazine compound. Peroxygen compound may also be present.

12 Claims, No Drawings

PROCESS OF CLEANING CLOTH

This application is a continuation-in-part of my copending application, Ser. No. 817,197, filed Apr. 17, 1969, now abandoned, and a continuation of Ser. No. 6,942, filed Jan. 29, 1970, now abandoned.

This invention relates to detergent compositions including an enzyme and an agent for improving the detergent effect.

Enzymes have been incorporated into detergent compositions since they are particularly effective against various common stains which are fixed to textiles and laundry. In particular, proteolytic enzymes, which possess the ability to digest and degrade protein matter, are effective in removing from textiles and laundry proteinic stains such as blood, sweat, milk, cocoa, gravy and other sauces and the like. This digestion or degradation of protein matter facilitates removal of dirt by the detergent.

In accordance with one aspect of this invention, a hydroxylamine compound or hydrazine compound is added to the enzyme-containing detergent composition. It is found that the presence of the hydroxylamine compound or hydrazine compound increases the effectiveness of the enzyme-containing detergent composition, both during the soaking step and the washing step.

The hydroxylamine compound or hydrazine compound may be employed in varying amounts. One suitable range is about 1 to 10 percent of the 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 anionic or nonionic properties. Anionic surfaces 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 about 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 caster oil and sulfated red oil; sulfated hydroxyamides such as sulfated hydroxy-ethyl 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 eight to 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, 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 six to 30 ethylene oxide units; condensation 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 mono-oleate and mannitan monopalmitate and the condensation products of polypropylene 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 diamine 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-amino-ethyl 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 one to three carbon atoms, including such one to three carbon alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen acetate, methosulfate, etc. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl stearyl ammonium chloride, trimethylcetyl ammonium bromide, methyl-ethyl-di-lauryl 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 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 formulation and the proportions therein.

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

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 about four to 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 about 80°C. and higher. They are also effective at ambient temperature and lower to about 10°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*.

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

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 percent 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 5 to 10 and at an alkaline pH of 8.5 to 9 they can withstand temperatures of 49°C to 77°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 differnet degrees of effectiveness in aiding in the removal of stains from textiles and linen.

The enzyme is preferably present in powdered form and is admixed into the detergent formulation. It is typically present in amount of about 0.001 percent – 4 percent by weight of the detergent composition, preferably about 0.05 – 1 percent, e.g., about 0.1 – 0.5 percent.

In addition to the materials described above, the detergent composition of the invention 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 ethanolammonium 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, borates, etc.

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 percent, with small amounts, e.g. 4–13 percent 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 pH 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 of about 50–90 percent by weight of the detergent composition.

The detergent composition may also contain additives such as sodium carboxymethylcellulose or polyvinyl-pyrollidone. These additives may be present in amount of about 0.1 percent – 5 percent by weight of the detergent composition. The detergent composition may also include minor amounts of optical brighteners, perfumes and preservatives. A peroxygen compound may also be present, such as sodium perborate in amount of, for instance, about 3 to 35 percent of the detergent composition. When peroxygen compound is present, it is best to use larger amounts of the hydroxylamine compound or hydrazine compound.

The hydroxylamine compound or hydrazine compound may be added as such or in the salt form, e.g. as the hydrochlorides, sulfates, nitrates, phosphates, flurosilicates, formates, or oxalates. Hydroxylamine, hydrazine, phenyl hydrazine, carbamoyl hydrazine, N-phenyl-N'-carbamoyl-hydrazine are examples of suitable compounds. When substituted hydroxylamine or hydrazine compounds are employed, they should retain at least one unsubstituted hydrogen on the hydroxylamine or hydrazine nucleus; thus, mono, di- or tri- substituted hydrazine may be used. The substituent, or substituents, may be alkyl, e.g. methyl or butyl, or aryl, e.g. phenyl, or of other types, e.g. carbamyl.

The following Examples are given to illustrate this invention further. All proportions therein, and elsewhere in this application, are by weight unless otherwise indicated.

EXAMPLE 1

This Example shows the effect of addition of hydrox-

ylamine hydrochloride to an enzyme-containing detergent composition, for both the soaking step and the washing step.

A. The soaking solution is a solution, in water, of (a) a commercial built synthetic detergent composition (described in detail below) in concentration of 5 grams per liter, (b) a commercially available proteolytic enzyme composition ("Alcalase") in concentration of 0.05 grams per liter, and (c) sodium perborate in concentration of 0.005 M. Where indicated, hydroxylamine hydrochloride is also present. Standard test samples of soiled cotton fabrics carrying substantial colored stain of protein nature (such as blood, sweat, milk, cocoa, gravy and the like, carrying carbon black pigment) are soaked in the soaking solution at room temperature for 60 minutes; 10 grams of soiled fabric are present per liter of soaking solution.

After the 60 minute soaking, the fabrics are removed from the solution (and then rinsed). The reflectance of the fabrics is then measured. An increase in reflectance indicates, of course, an improvement in the cleanliness of the samples.

The following tabulation shows the improvement obtained by the hydroxylamine hydrochloride:

concentration of $NH_2OH \cdot HCl$ (in mols per liter)	0	0.0001	0.0004	0.001
reflectance	18	19	20	21

B. For the washing step the previously soaked fabric is immersed in a fresh solution identical with that used for the soaking step and washed (with periodic agitation) for 30 minutes at about 100°C.; 10 grams of soaked soiled fabric are present per liter of washing solution.

The following tabulation shows the improvement obtained by the inclusion of various amounts of hydroxylamine hydrochloride in the solution:

concentration of $NH_2OH \cdot HCl$ mols per liter)	0	0.001	0.004
reflectance	23	25	29

EXAMPLE 2

In this Example, an enzyme-containing soaking solution identical with that of Example 1A is employed, except that no perborate is present. The soaking conditions are the same as those of Example 1A.

The following tabulation shows the improvement in reflectance obtained by the inclusion of various amounts of hydroxylamine hydrochloride in the solution:

concentration of $NH_2OH \cdot HCl$ (in mols per liter)	0	0.005	0.001
reflectance	39	40	42

EXAMPLE 3

Example 1 is repeated using hydrazine sulfate in place of the hydroxylamine hydrochloride. The following results are obtained:

Concentration of Hydrazine sulfate (in mols per liter)	Reflectance after soaking step	Reflectance after washing step
0	21	24
0.0001	21	26
0.0002	21	26
0.0004	22	26
0.0006	22	31
0.0008	23	30
0.001	22	29
0.002	21	29
0.004	25	36
0.006	24	34

The commercial detergent composition used in Examples 1–4 has the following composition:

	%
sodium dodecyl benzene sulfonate	17.5
sodium tripolyphosphate	26.5
sodium silicate (1:2 SiO_2: Na_2O mol ratio)	6.0
sodium carboxymethylcellulose	0.8
optical brightener	0.2
perfume	0.2
preservative	0.004
moisture	15
sodium sulfate	q.s. to 100

The proteolytic enzyme Alcalase used in Examples 1–4 is characterized as having its maximum proteolytic activity at a pH of 8–9. This activity is measured on the commercial enzyme available from Novo Industri A/S, Copenhagen, Denmark is about 1.5 Anson Units per gram of the enzyme. The commercial enzyme is a raw extract of bacillus subtillis culture and contains about 6 percent of pure crystallized proteolytic material.

EXAMPLE 4

In this Example soiled fabric carrying proteinic stain is soaked for 60 minutes at room temperature in a solution containing 0.05 percent Alcalase, 0.0062 mol per liter of sodium perborate and 5 g liter of the commercial detergent composition in water together with 0.002 mol per liter of one of the compounds listed in the table below. The soaked fabric is then washed (with periodic agitation) in a fresh solution of the same composition as the soaking solution for 30 minutes at 95°–100°C.

The results are expressed in the turbidity of (a) the used soaking solution, (b) the turbidity of the used washing solution and (ab) the sum of these two turbidities. An increase in turbidity of the solution has been found to indicate that more of the soil has been transferred from the fabric to the solution during use.

In making the turbidity tests the proteins in the liquid are first precipitated by addition of sulfonic acid and the optical density of the resulting dispersion of proteins is measured using light whose wavelength is 405 m.

Two types of soiled fabrics are used: one is soiled with chocolate and the other (designated in the table below as ("biosoil") is the same as that used in Example 1.

Additive	Stain	Turbidity *a*	*b*	*ab*
none (control)	chocolate	9	11	20
phenyl hydrazine hydrochloride	"	17	23	40
hydrazine sulfate	"	9	19	28
N-phenyl-N-'carbamyl-hydrazine (C_6H_5—NH—NH—CO—NH_2)	"	10	18	28
hydroxylamine sulfate	"	12	14	26
none (control)	biosoil	23	20	43
phenyl hydrazine hydrochloride	"	33	26	59
hydroxylamine sulfate	"	32	23	55
hydrazine sulfate	"	27	28	55
N-phenyl-N'-carbamyl-hydrazine	"	31	24	55
N-carbamyl-hydrazine hydrochloride	"	23	24	47

As is well known, sodium perborate is available commercially in two forms, the monohydrate and the tetrahydrate. This invention is useful with both these forms. In the foregoing Examples the tetrahydrate form of the

sodium perborate is used. Excellent results are also obtained when the monohydrate form is employed.

It is understood that many variations may be made herein without departing from the spirit of the invention.

I claim:

1. A process of cleaning cloth comprising treating said cloth with water containing a detergent composition consisting essentially of an organic water-soluble detergent and a proteolytic enzyme effective at a pH range of about four to 12 and a compound selected from the group consisting of a hydroxylamine compound and a hydrazine compound, each compound having at least one unsubstituted hydrogen on the hydroxylamine or hydrazine nucleus of said compound, said detergent being selected from the group consisting of anionic, nonionic and cationic detergents, said composition containing about 5 to 95 percent by weight of said detergent, about 0.001 to 4 percent by weight of said enzyme and about 1 to 10 percent by weight of said compound.

2. A process of cleaning cloth as in claim **1** in which the organic detergent is an anionic surface active agent.

3. A process of cleaning cloth as in claim **1** in which about 50 to 90 percent by weight of a water-soluble inorganic builder salt is also present.

4. A process of cleaning cloth as in claim **1** in which about 50 to 90 percent by weight of an organic sequestering agent is also present.

5. A process of cleaning cloth as in claim **1** in which said compound is a hydrazine compound.

6. A process of cleaning cloth as in claim **1** in which said compound is a hydroxylamine compound.

7. A process of cleaning cloth as in claim **1** in which said compound is phenyl hydrazine.

8. A process of cleaning cloth as in claim **1** in which said compound is N-phenyl-N'-carbamyl hydrazine.

9. A process of cleaning cloth as in claim **1** wherein said cloth is soaked in water containing said composition and then washed in water containing said composition.

10. A process of cleaning cloth as in claim **1** in which sodium perborate is also present in said composition in amount of about 3 to 35 percent by weight.

11. A process of cleaning cloth as in claim **6** in which said compound is hydroxylamine sulfate.

12. A process of cleaning cloth as in claim **9** wherein said cloth is soaked in water containing said composition and then washed in water containing said composition.

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